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DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

Twenty-Fourth Six-Month Report
for the period
1 January 1975 to 30 June 1975

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I: INTRODUCTION, ABSTRACT, AND SUMMARY

This report will cover the work performed from 1 January 1975 through 30 June 1975 on Grant NGL 03-002-019 between the University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially, the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere and adsorption system for control and separation of gases.

Results to date have included detectors for O_2 and H_2 under partial vacuum conditions (Publications 1, 3, 4). Experiments on detectors for use at high pressures began in 1966; and systems for CO , H_2 and O_2 were reported in 1967 and 1968 (Publications 8, 11). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semiconductor material could be electrically cycled to adsorb and desorb a specific gas. This work was extended to obtain quantitative data on the use of semiconductors as controllable adsorbents (Publications 11, 12).

In 1968 a new technique for dry replication and measurement of the thickness of thin films was developed. A commercial material, Press-O-Film, was shown to be satisfactory when properly used. This technique is most useful for studies of semiconductor thin films where normal interference techniques are not practical because of the non-reflective nature of the film (Publication 13).

During the period from 1968 through 1971 the Carbon Monoxide Detector, first demonstrated on the NASA program (Publication 8), was refined and improved for use by the Department of Health, Education and Welfare.

In 1969 studies began on a Corona Discharge Detector for water vapor. This system was shown to be rapid in response, suitable for continuous operation, and reasonably linear in output (on a logarithmic plot) from 10 percent relative humidity to 95 percent relative humidity. A program to develop this detector for hydrological applications began in 1970 but was temporarily dropped because of limited user interest.

In 1970 we began an investigation of the catalytic oxidation of various gases, i.e., CO, NH₃ and H₂ over metallic catalysts. We demonstrated that the rate of reaction could be observed and controlled in terms of the exoelectron emission from the catalysts (Publication 16). In 1971 this study was directed to the expanded monel metal catalysts used for auto exhaust emission control and for spacecraft atmospheric purification (Publication 20).

This investigation has been extended to catalysts operating at ambient (one atmosphere) pressure and to the dispersed metal-ceramic catalysts used in the chemical industry. There seems to be no question that the exoelectron effect can be used to monitor catalyst operation.

The capability of monitoring the actual rate of catalysis is important in many industrial operations where a slight change in rate-of-reaction can have a significant effect on the safety or economics of the process. The conventional techniques, which involve analysis of the

reactant or temperature control of the catalyst, are frequently too slow to permit accurate control. Application of this control technique has been discussed with the Dow Chemical Company (Texas Division).

Another application of the exoelectron effect exists in the area of catalytic research. An understanding of the mechanism relating catalysis to electron emission will help in obtaining a final explanation for the catalytic process itself.

In 1971 we began the study of a new technique for analysis of solid materials. This system involved heating or grinding the substance and observing the induced exoelectron emission. The effect is known as Temperature Stimulated Exoelectron Emission (TSEE). One application of this phenomenon to observation of grinding processes has been published (Publication 18).

In 1973-74 we began investigating the electrostatic charging phenomena that are associated with the generation of dust particles. These charge effects may be an important factor in the atmospheric suspension of dust during dust storms. This may be particularly significant in the Martian dust storms where the low atmospheric density will not support the wind-raised dust clouds, observed on earth.

Other aspects of this dust investigation relate to an understanding of dust levitation on the moon. Recent lunar observations suggest that a significant amount of dust is associated with the terminator. This dust suspension can only be understood in terms of electrostatic phenomena.

Two other applications of this work exist in areas related to Industrial health:

1. Possible correlations between dust charging phenomena and the effects of the dust on the human lung. A publication on this work was submitted to the Journal "Biochemistry" in March 1975.
2. The removal of electrostatically charged dust by means of a water fog charged to the opposite polarity.

Both of these topics were investigated in 1973 and the work on topic 2 is continuing. There are some significant electrostatic phenomena associated with industrial health.

In 1974 we began an investigation of the optical and electrostatic phenomena associated with the compressive failure of rocks and minerals. This work has a direct application to the transient lunar phenomena that have been reported by many observers. These lunar effects appear as obscurations of lunar features or as flashes of light during the lunar night. It has been suggested that the obscuration effects are due to gases leaking from freshly fractured rock while the light emission occurs when electrons, from the fractured rock, ionize the gases. Investigation of this phenomena is continuing.

SUMMARY OF WORK IN THE PAST YEAR AND STUDIES PLANNED FOR THE NEXT TWELVE MONTHS

Electrostatic Charging of Dust and Its Effect on Planetary Atmospheres

In our last report we discussed the design of a grinding system, dust chamber and impaction sampler for measurement of dust charge versus

diameter. The impaction sampler is shown in Figure 1, typical data obtained with this device is shown in Figures 2 through 11. This data indicates that the smallest (one micron) particles are negatively charged and we might note that this has been observed with every material tested, to date, with the exception of magnetite.

This suggests that natural dusts may acquire a charge as they are blown about by the wind and that the one micron particles might well be levitated by the electrostatic field of the earth. This field has a positive gradient (earth negative) and would effectively levitate negatively charged particles. In this connection it is worth noting that the "permanent" atmospheric impurities are in the range of 0.1 to 1 micron in diameter [1]. Spheres of this size range would be normally expected to settle out of the atmosphere at a speed of some 12.6 cm/hr. The fact that these impurities are observed to remain suspended almost indefinitely suggests the electrostatic levitation is involved.

Other phenomena that indicate the existence of electrostatic levitation in the earth's atmosphere have been reported by various observers and reviewed by Israel [2]. In several cases (page 453) the existence of a heavy haze layer was associated with a large negative charge at the same altitude. This effect seems to be especially related to atmospheric inversions and may well be partially responsible for the high concentration of dust under inversion conditions.

If atmospheric dust is electrostatically charged we must expect that in a "low wind" situation charge separation will occur, with positive charges accumulating near the earth and negative charges at some

higher altitude. This has been observed by many meteorologists and is often called the "electrode effect." One reference [3] reported 1000 negative charges per particle at altitudes of 50, 65 and 80 km.

Effects of a similar type have been observed during the massive dust storms called "haboobs" in Arabic. These storms produce huge changes in the normal electrostatic field of the earth and it is generally assumed that this is due to a layer of negative charge at the top of the dust cloud and positive charge near the ground [4]. Once again this indicates that electrostatic levitation is present, and it has been noted that the dust raised in these storms is very slow to fall-out.

It has been suggested that the formation of a haboob is necessary to precipitate the summer monsoon season because it raises charged particles to high altitude. The correlation between dust storms and summer rain is well known in Arizona and has been reported from Khartoum [5].

All of the above suggests that charged particles may have a significant effect on the earth's atmosphere. It follows then that an understanding of the dust charging and levitation phenomena is necessary if we are to untangle the dynamics of the lower and middle atmosphere.

Applications to Mars

Typical average conditions on Mars are assumed to be:

$$T = 200K, P \text{ (surface)} = 6.1 \text{ TORR (mm of Hg)} .$$

The normal rate-of-fall under Stokes Law (for spheres of unit density) is:

$$C\left(\frac{\text{cm}}{\text{sec}}\right) = \frac{2 R^2 g}{9\eta}$$

Here g is the gravitational acceleration (cm/sec^2) R is particle radius and η is viscosity. Using this data and appropriate values for g and η we obtain (for 1 micron particles)

$$C = 1.73 \cdot 10^{-3} \text{ cm/sec.}$$

This is quite close to the values of $3.56 \cdot 10^{-3} \text{ cm/sec}$, for the same particles in the earth's atmosphere. We can expect that the Stokes Law effects on Mars are very similar to those on earth.

Turning to the question of how dust is raised by the wind we note that the dynamic wind pressure on a sand grain will be proportionate to $1/2 \rho v^2$ where ρ is the gas density. On Mars ρ is almost 100 times lower than the value on earth and this suggests that very high winds would be required to raise dust storms on Mars. Calculations of this type have been made by Ryan [6] and refined by Sagan [7]. Reference 7 suggests that velocities of 300 km/hr might be required and refers to one telescopic observation of a Martian Dust cloud moving at 100 km/hr.

We suggest that these wind velocities are unlikely to occur very often, especially in view of the heavily cratered Martian surface. It seems more reasonable to suggest that low velocity Martian winds move the surface material about and induce electrostatic charging. The very

dry environment and low ambient pressure would encourage this type of phenomena. One laboratory study [8] has indicated that significant charging occurs when a sand/dust mixture is agitated under simulated Martian conditions. We suggest that this local agitation and charging of dust induces levitation which allows the dust to move upward in the Martian atmosphere.

We hope to investigate the effects of this type in the coming year with emphasis on two questions: (1) Electrostatic charging under simulated Martian conditions, and (2) Measurement of vertical dust profiles in the 3' x 3' x 3' dust chamber. The electrostatic charging studies will be started in a one gallon plastic jar that will be turned on a small rock tumbler. The system is shown in Figure 12, initial charge measurements will be done by means of a charge detector inserted in the jar. At a later date a glass container, that can be held at 6 to 10 torr, will be used. It will be important to determine the agitation required for charging and the effect of impurities, humidity, etc.

The dust profile studies have been under way for the past 6 months, typical results are shown in Figures 13 and 14. This data was taken with the impaction sampler shown in Figure 1. This unit separated the dust into six size ranges and it is clear in Figure 13 that some 30 minutes after injection the larger (5.8 micron) particles had essentially "fallen out," while the respirable particles from 0.54 to 1.6 microns had only been reduced by some 50%. This is in agreement with the many reports of permanent atmospheric impurities in the one micron size range.

We should note that this data was obtained with an impaction sampler drawing from just one level in the dust chamber. To observe the dust density, versus height, we made use of the optical system discussed in our last report. Typical results of this study are shown in Figure 14. Here the total optical dust density is plotted versus height in the dust chamber, as a function of time after injection. The initial profile, after some three minutes, shows a more or less constant dust density with height. The increase over the $t = 0$ value is due primarily to dust falling from the upper part of the chamber. After some 21 minutes the density at the lowest level had increased to a small degree while the density at the one foot height had been greatly increased. This suggests that the dust is levitated at this level.

The optical system used for these studies did not permit a measurement of the dust density above the one foot level and we decided to repeat these experiments with a charge detection scanner that could move vertically from the bottom to the top of the dust chamber. This system is shown in Figure 15. We decided to sense the local field gradient rather than the optical density because of the difficulties we experienced in keeping the optical system clean.

The scanner shown in Figure 15 carries a Trek Corporation (Gasport, New York) charge detector system. This system is well suited to planetary experiments where the usual mechanical "field mills" might be subject to jamming by dust in their bearings. The Trek unit has no moving parts and can be used for observation of either charge or field gradient with the installation of a small adapter. The output is 0-100 volt DC (at

10 ma) and is quite suitable for conversion to a pulse code for radio transmission.

Our most recent results with the Trek unit (in the voltage gradient mode) are shown in Figures 16 and 17. For this study a 3' x 3' metal base plate was installed in the dust chamber and connected to a DC power supply. This provided a controllable field gradient in the chamber.

Typical results with no dust in the chamber are shown in Figure 16 (light weight lines) for the plate grounded and ± 250 volts. At 65 cm altitude the effect of the field plate has disappeared. The heavier lines in Figure 16 show the effect of adding freshly ground negatively charged silica dust (the system is allowed to stabilize for 15 minutes after the dust is introduced). The grounded plate data shows a slight increase in charge at the 40-45 cm level which may be due to the residual effect of the earth's (normally negative) potential. With the plate at - 250V the negatively charged dust is levitated to the top of the chamber while with + 250 volts, on the plate, the dust moves downward.

This is shown more dramatically in Figure 17 where the "no dust" data has been subtracted from the results of Figure 16. The + 250 volt curve is almost straight, dust has been drawn down toward the plate effectively neutralizing the field of the plate itself.

With a grounded plate the highest dust concentration was observed at some 40-45 cm altitude. This is shown very clearly in Figure 17 and may represent the altitude at which a particular fraction of the dust comes into equilibrium between the forces of gravity and the earth's electrostatic field.

At - 250 volts we observe two peaks in the field gradient at 40 and at 55 cm. The very rapid change in field gradient from 20 to 37 cm has been observed several times under these conditions and we suggest that it is related to the decay of the field induced by the charged plate. Figure 16 indicates that at 35 cm the no-dust field has fallen to some 50% of the value at 20 cm. The high field gradient at 35-40 cm (in Figure 17) and the increase from 20 to 35 cm (in Figure 17) may be due to the levitation of some rather large (5 to 10 micron) particles at the 35 cm level. It would follow then that the peak at 55 cm (in Figure 17) might be due to 0.5 to 3 micron particles levitated at this high elevation.

All of the above data is consistent with our suggestion that dust levitation can be observed in the laboratory. We note that the voltage gradients observed (45 volts/cm) are comparable to those reported in dust storms [2,9] indicating that levitation will occur in the earth's atmosphere.

At this point we might note that the dust distribution in the chamber at + 250 volts is not the same as that at 0 or - 250 volts. At + 250 volts the 5 to 10 micron, negatively charged particles fall-out very quickly and after 15 minutes the dust population is largely in the 0.5 to 2 micron range. In contrast, at - 250 volts the 5 to 10 micron particles may remain in suspension producing the peak observed in Figure 17 at 55 cm. A schematic representation of the data of Figure 17 is shown in Figure 17a. We feel that this may clarify the situation in the dust chamber.

In the next 6 months we proposed to continue and extend this work. Dust size determinations will be made at specific altitudes in the dust chamber under known voltage gradient conditions. This will allow us to prove that the particulate stratification suggested above, really occurs. Other dusts, i.e. clay, shale will be used to see if similar effects can be obtained. If possible we hope to begin observing the effects of relative humidity on these processes.

Experimental Studies from a Martian Lander Vehicle

A review of the field experiments in dust storms and the laboratory work of various investigators indicates that the parameters of interest on Mars would include:

1. Pressure, temperature and relative humidity.
2. Wind velocity and direction.
3. Particulate size and composition.
4. Electrostatic charge and field gradient.

Ideally we would like to measure these parameters from the surface of the planet to an altitude of several thousand feet (2 km). However, we recognize that an experiment of this scale is hardly practical on earth to say nothing of Mars.

It seems more reasonable to suggest that an instrument package be raised some 12 meters from the surface on an extendable boom of the type manufactured by Hunter Spring (Hatfield, Pennsylvania) or Spar Aerospace (Toronto, Canada). Devices of this type have been used to erect the sunshield on the Apollo Lunar Surface Package. As the boom

moved upward it could be stopped periodically to allow measurements to be taken. The fully erected boom could serve as a transmitting antenna after deployment, thereby saving weight in the total system. Raising the instruments to a height of 12 meters would put them out of all possible boundary layer effects and allow a measurement of atmospheric parameters under essentially "free stream" conditions.

Instrumentation for Planetary Studies

Various instruments for measurement of temperature, wind velocity and relative humidity are available and could be easily adapted for a Mars Lander. Pressure measurements would be done with a diaphragm pressure gauge with a built-in transistor read-out circuit.

Measurement of the total dust content, sized below 10 microns, might be done with a beta-ray adsorption system of the type manufactured by the GCA Corporation (Bedford, Massachusetts). This unit separates the dust into fractions above and below 10 microns, in a small cyclone, and deposits them under 10 microns of dust on a greased slide. The dust adsorbs incident beta radiation and the degree of adsorption is a measure of the quantity of dust-in-the-atmosphere. The slide turns automatically between measurements and some 90 tests can be made before the slide has to be cleaned.

Observations of the charge level and the field gradient would be made with a modified Trek Detector. Conversion from measurement of charge to observation of field gradient would involve swinging an adapter in front of the probe.

A series of measurements of these parameters would be a major step toward understanding the Martian environment.

Surface Catalysis and Exoelectron Emission

This program is an outgrowth of our earlier studies of gas-surface interactions with the mass spectrometer. We have shown that as soon as catalytic oxidation of CO, H₂ or NH₃ begins (on hot platinum), there is emission of nonthermal exoelectrons. This "exoelectron" emission can be used to monitor the rate of catalysis. Suppression or enhancement of this exoelectron emission results in an increase or decrease in the rate of catalysis itself. A paper on this topic has appeared in the Journal of Catalysis (see Publication 16).

In another study we followed the catalytic reaction of NO with CO over hot monel. Monel is the candidate metal for a reaction to remove NO_x from automotive exhaust gases, and we have demonstrated that the rate of reaction can be monitored in terms of exoelectrons emitted by the catalyst. A short paper discussing our results has appeared in the Journal of the Society of Automotive Engineers (Publication 19).

In a more recent work we observed the exoelectron emission associated with the oxidation of CO and CH₄ at atmospheric pressures. The reactor-catalyst system is shown in Figure 18 (repeated from our earlier reports) typical results are shown in Figures 19, 20 and 21. Figure 19 shows an excellent correlation between the rate of oxidation (of CH₄) and the exoelectron current, versus temperature. There seems to be no question that the EEE current could be used to monitor this catalytic process.

Similar conclusions for CO oxidation can be drawn from Figures 20 and 21. Here oxygen was used in place of air because of the lower reactivity of CO. The higher temperatures, required for this reaction, induced some thermal electron emission and for this reason the k and I_e curves of Figure 20 are not parallel. If we correct for this thermal emission by subtracting the I_e values observed at 0% CO we obtain the data of Figure 21. The parallelism of the I_e and k curves in Figure 21 is obvious suggesting that exoelectron emission can be used to observe catalytic reactions at atmospheric pressure. (A letter publication on this work will be sent to the Journal of Catalysis in August 1975.)

The studies of dispersed catalytic reactions have emphasized the oxidation of ethylene, to ethylene oxide, over a silver catalyst supported on an alumina substrate. The catalysis assembly is shown in Figure 22, the reaction is run in the vacuum system to allow use of the mass spectrometer. The reaction itself is quite exothermic and operation under partial vacuum conditions (10^5 torr) provides a significant measure of safety.

Typical results are shown in Figure 23 where we have plotted the catalyst temperatures, gas compositions and exoelectron emission versus time. The correlation between changes in temperature and exoelectron current (I_e) is excellent especially at $t = 16$ min where the reaction stabilizes. A similar effect is observed at 32 minutes when the catalyst heater is turned off. We suggest that these effects are due to changes in temperature and the rise in I_e at 16 minutes may well be due to an

en dothermal adsorption phenomena that disturbs the catalyst surface. We propose to investigate this effect in more detail in the next six months.

The data of Figure 23 shows the effects of the reaction as a decrease in the partial pressure of oxygen P_{O_2} and an increase in the partial pressure of ethylene oxide $P(CH_2)_2O$. This is shown more clearly in Figure 24 where we have plotted the reaction coefficient (k) and the exoelectron current I versus temperature. K was taken as the ratio,

$$K = \frac{P_{(44)}(T \text{ } ^\circ K)}{P_{(44)}(T=273^\circ K)}$$

Once again the correlation, in terms of the slope of K versus that of I, is excellent suggesting that the exoelectron current is potentially valuable for monitoring catalytic reactions.

Our future plans in this area include the rebuilding of the catalyst-mass spectrometer set up to permit faster response. At the same time the use of our gas chromatograph will allow positive separation of CO_2 and $(CH_2)_2O$. The need for a system of this type may be seen by examining Figures 25 and 26, typical mass spectrometer runs for this reaction. Figure 25 was run with the catalyst at ambient temperature, while the data of Figure 26 was obtained at $274^\circ C$. The growth in the mass 44 and the mass 30 peaks, with temperature, is quite obvious and we suggest that the mass 44 peak is $(CH_2)_2O$ rather than CO_2 for two reasons:

1. First the existence of a prominent peak at mass 22, $(\text{CH}_2)_2\text{O}^{++}$, the height of this peak is well correlated with the growth of a mass 44 peak. The second ionization of $(\text{CH}_2)_2\text{O}$ is a process that occurs quite easily and this adds to our belief that the 44 peak is $(\text{CH}_2)_2\text{O}^+$.
2. Second, the differences in the spectra when CO_2 is introduced into the system. Typical CO_2 spectra do not show a half mass peak at $\frac{m}{e} = 22$ because of the high energy required for the second ionization of a CO_2 molecule.

In the next 6 month period we plan to have both the gas chromatograph and the mass spectrometer in operation. This will remove all ambiguity about the composition of the gases in the system.

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PERSONNEL

Students who have been supported by the grant and their present activities are listed below:

1. Donald Collins, M. S., 1963, Ph.D., California Institute of Technology, September 1969. Presently Research Associate, CIT.
2. George Rozgoni, Ph.D., 1963; Senior Staff Member, Bell Telephone Laboratories, Murray Hill, New Jersey.
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S. A. Hoenig, et al

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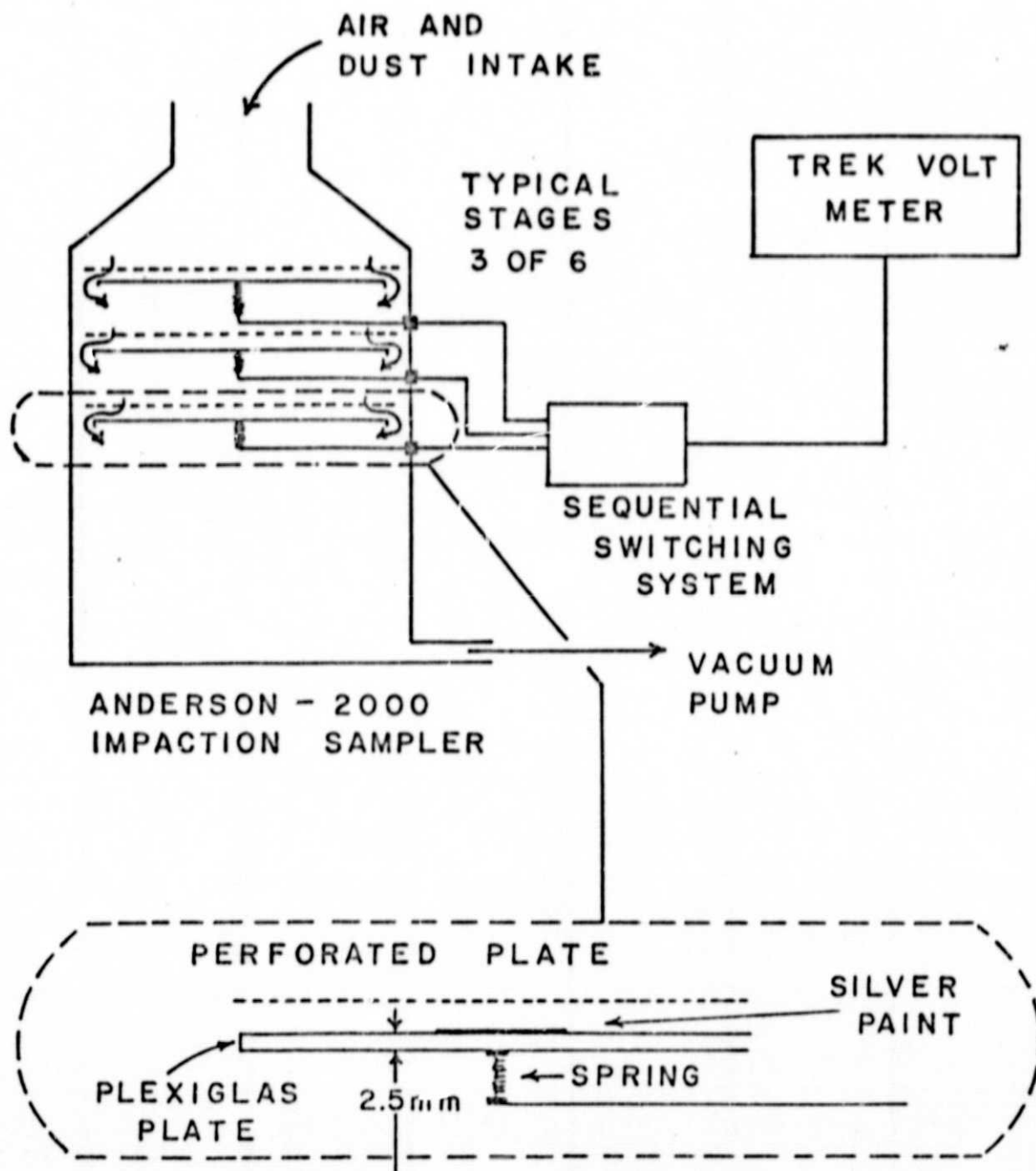
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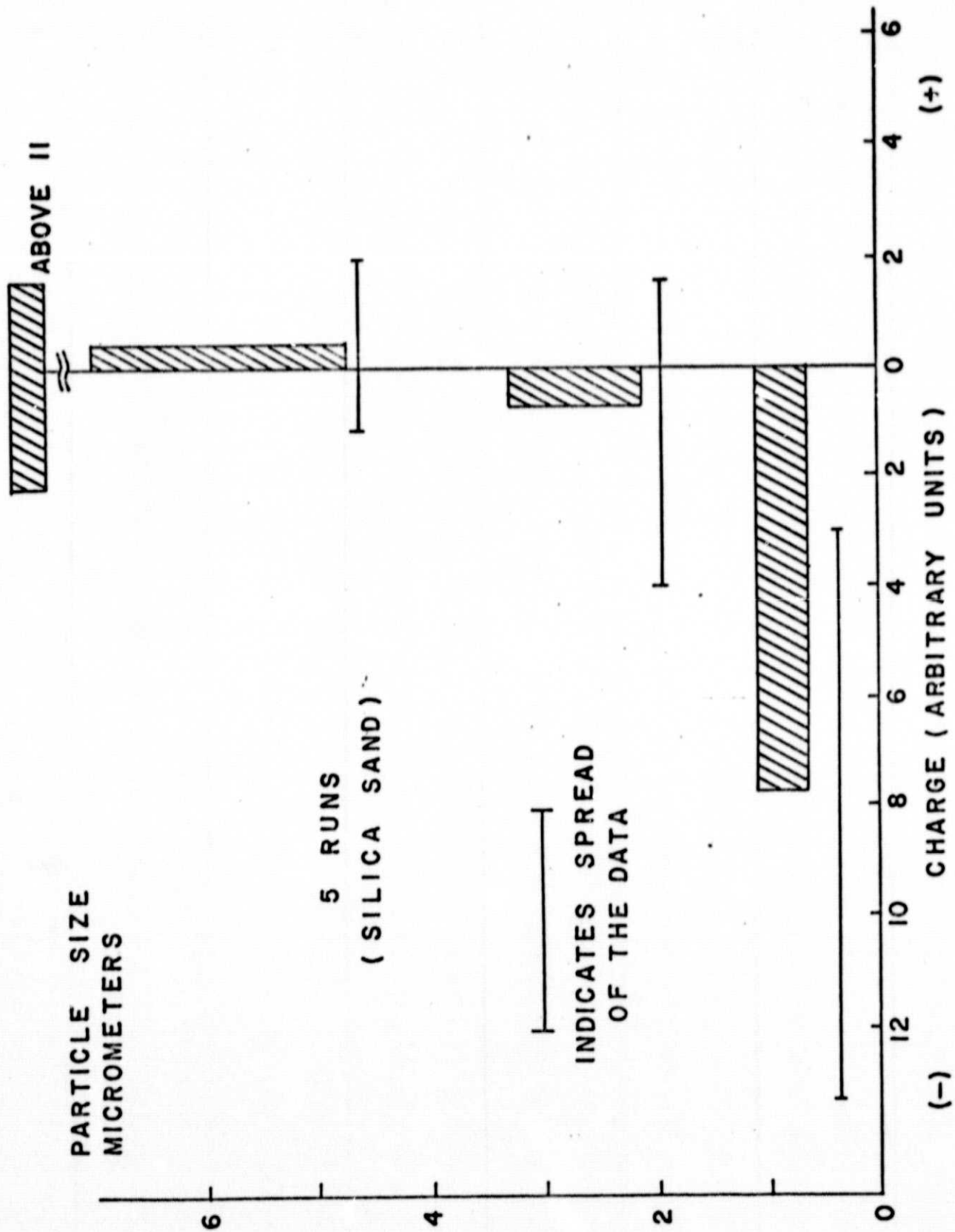
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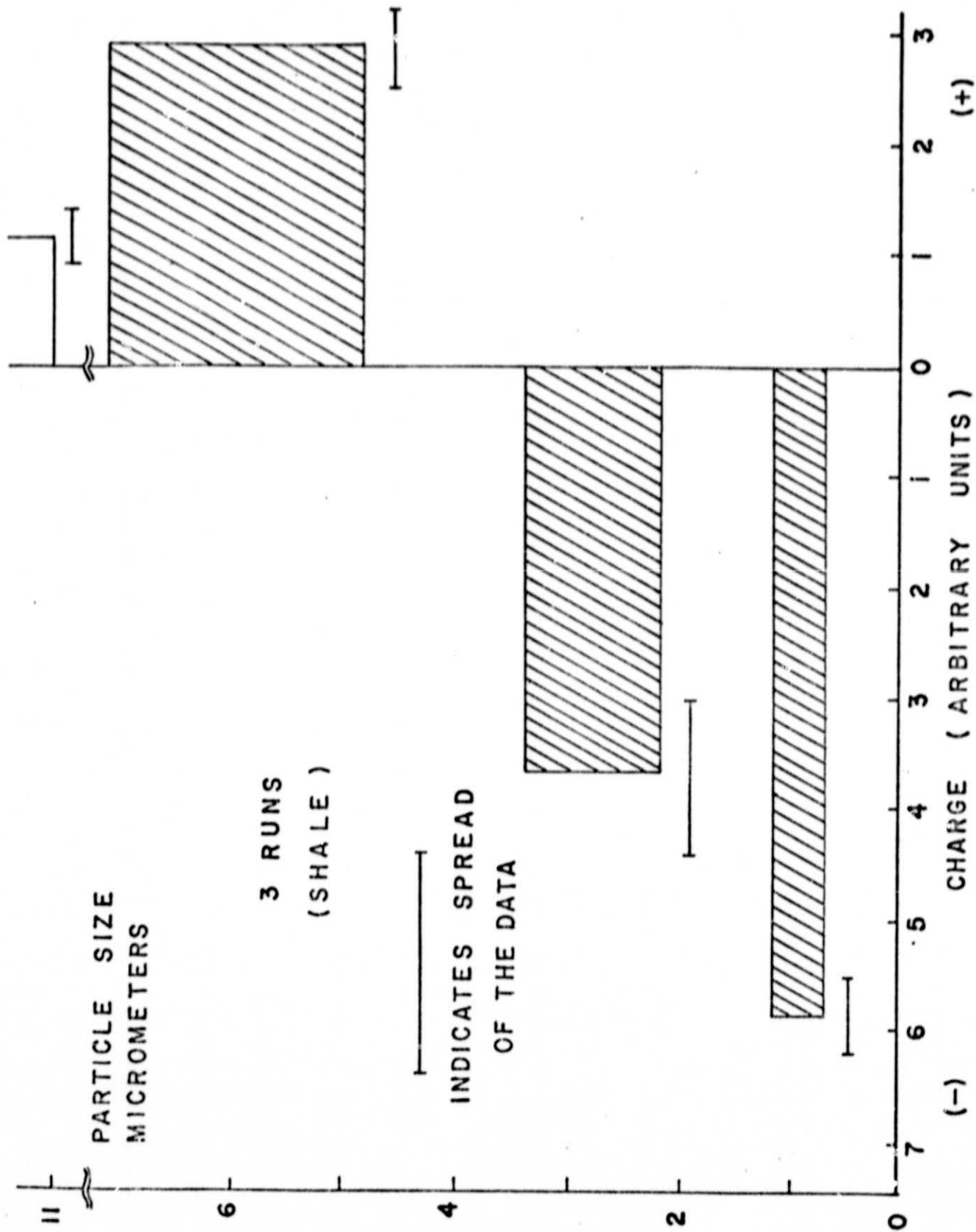
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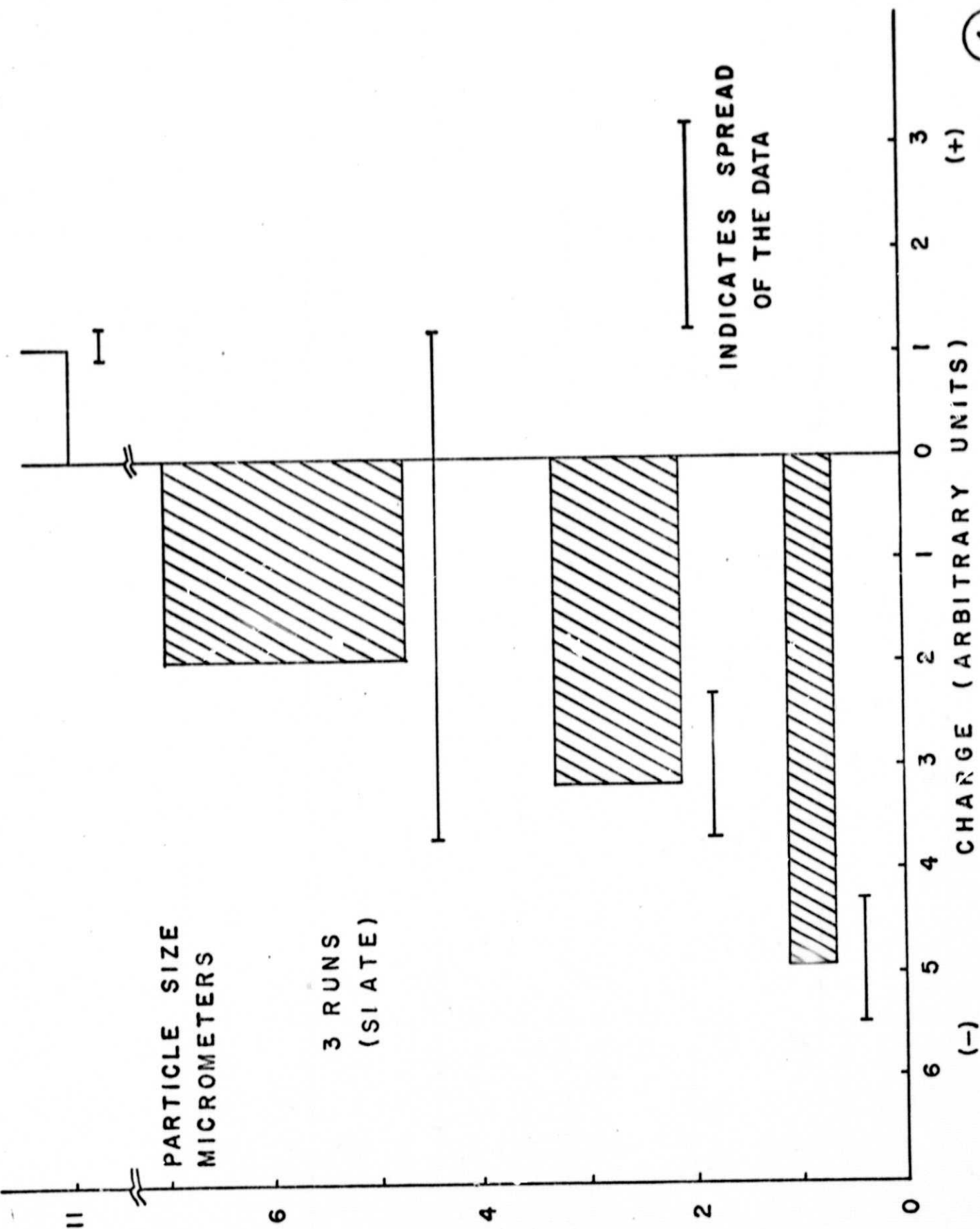
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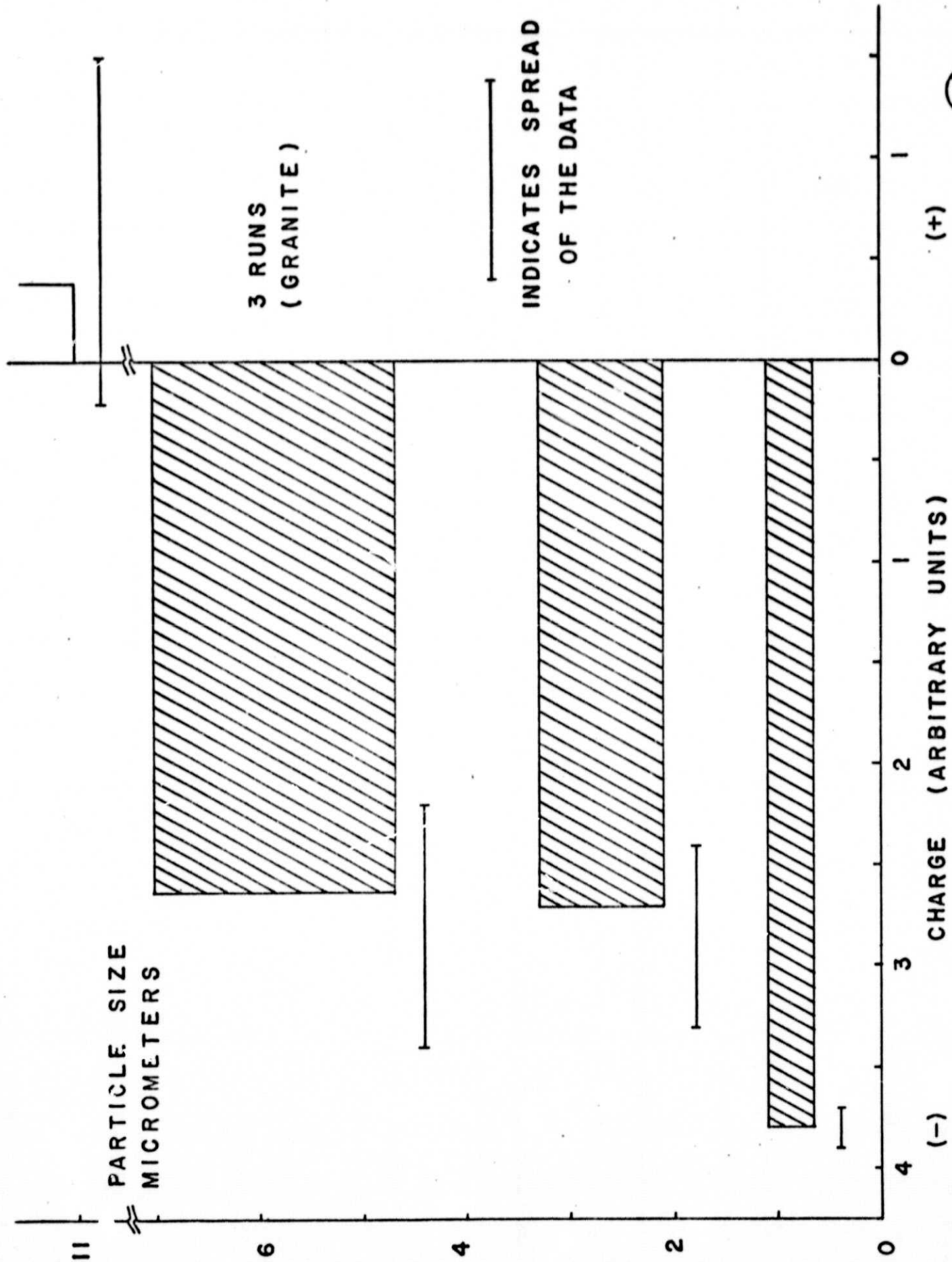
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23. Pressure, Temperature and Exoelectron Current Versus Time (Reaction of $(\text{CH}_2)_2 + \text{O}_2$ Over Silver)
24. Reaction Constant (K) and Exoelectron Current (I) versus Temperature (Oxidation of Ethylene Over a Dispersed Silver Catalyst)
25. Mass Spectra of $(\text{CH}_2)_2 + \text{O}_2$ Over a Silver Catalyst (Room Temperature)
26. Mass Spectra of $(\text{CH}_2)_2 + \text{O}_2$ Over a Silver Catalyst (274°C)

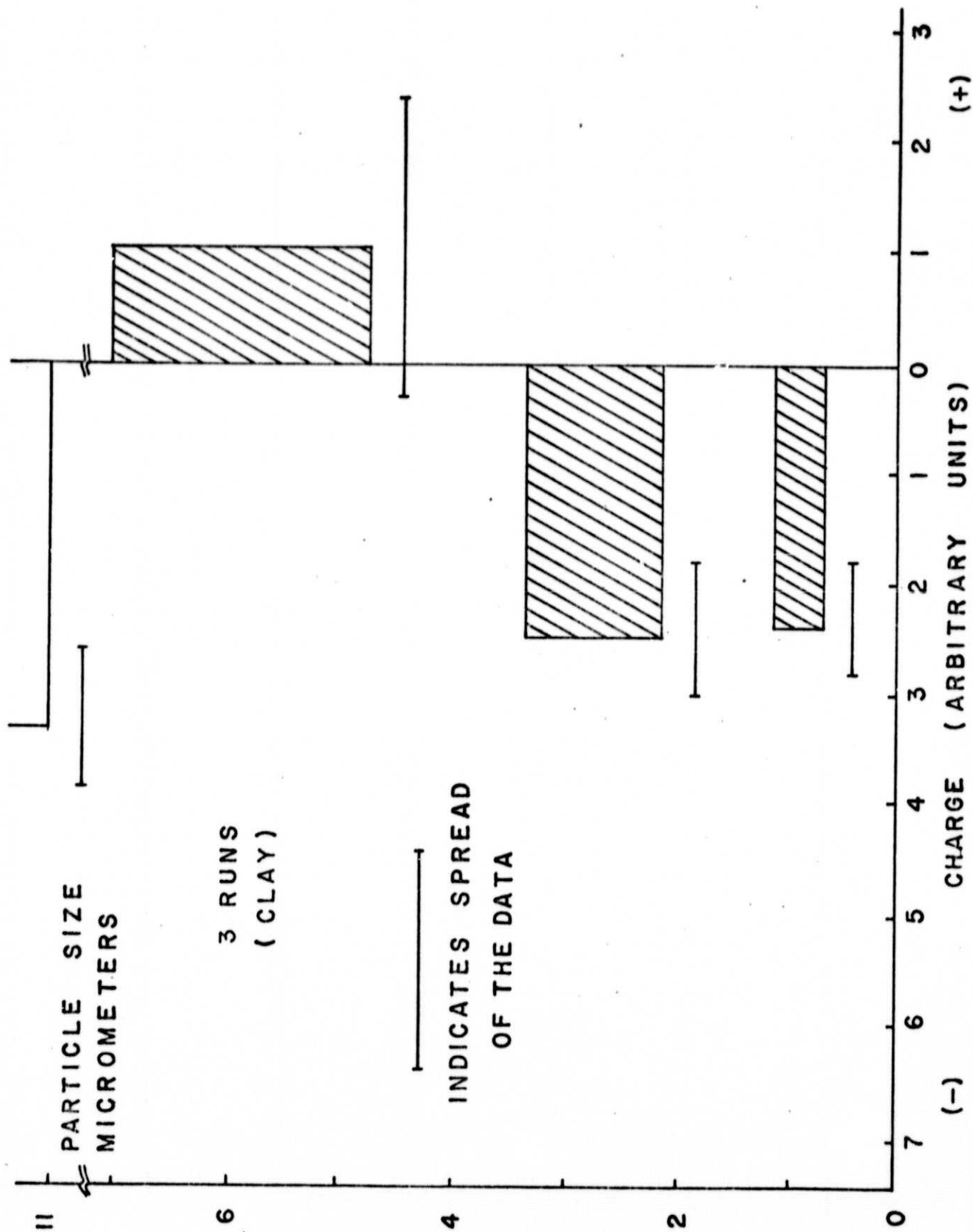


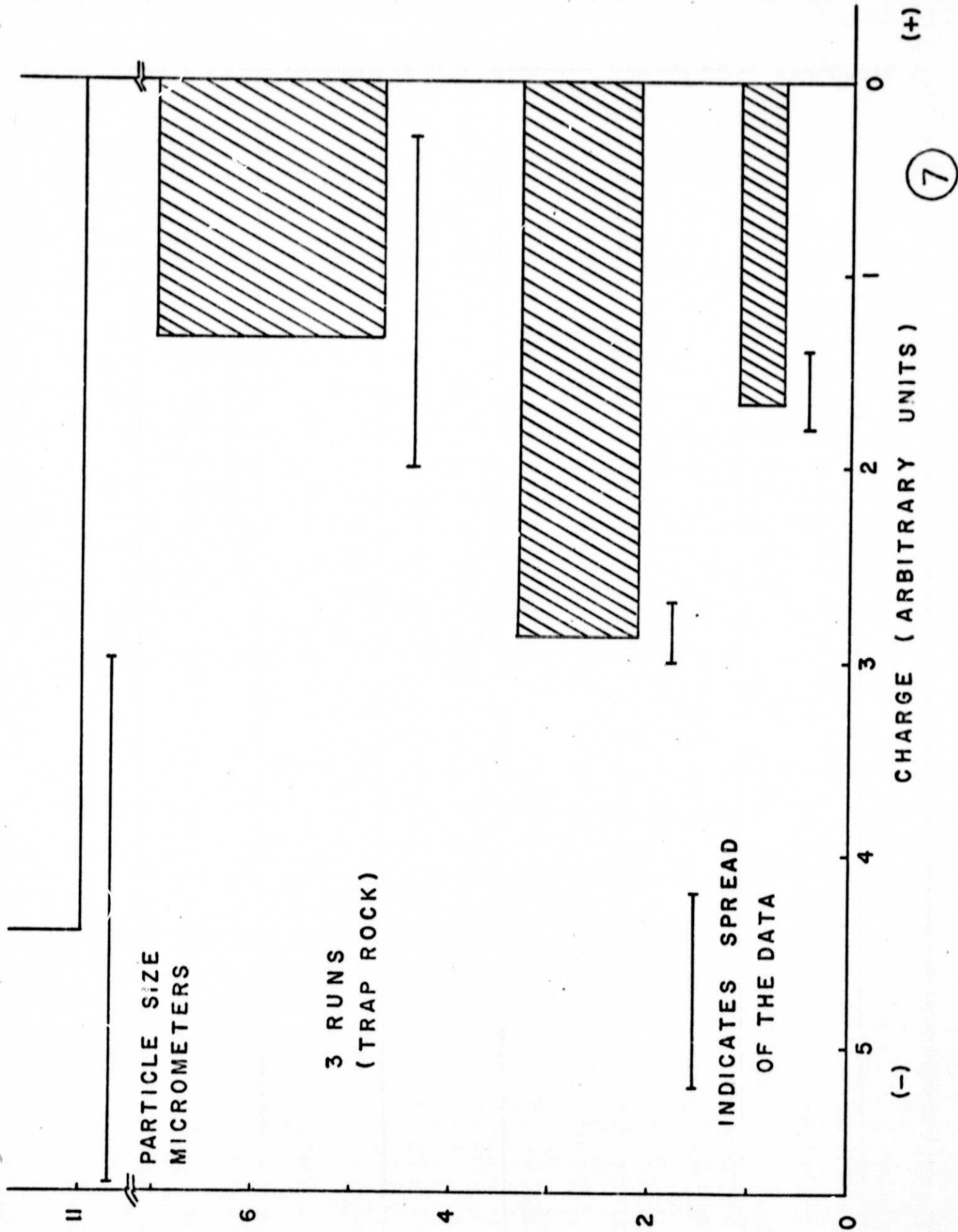


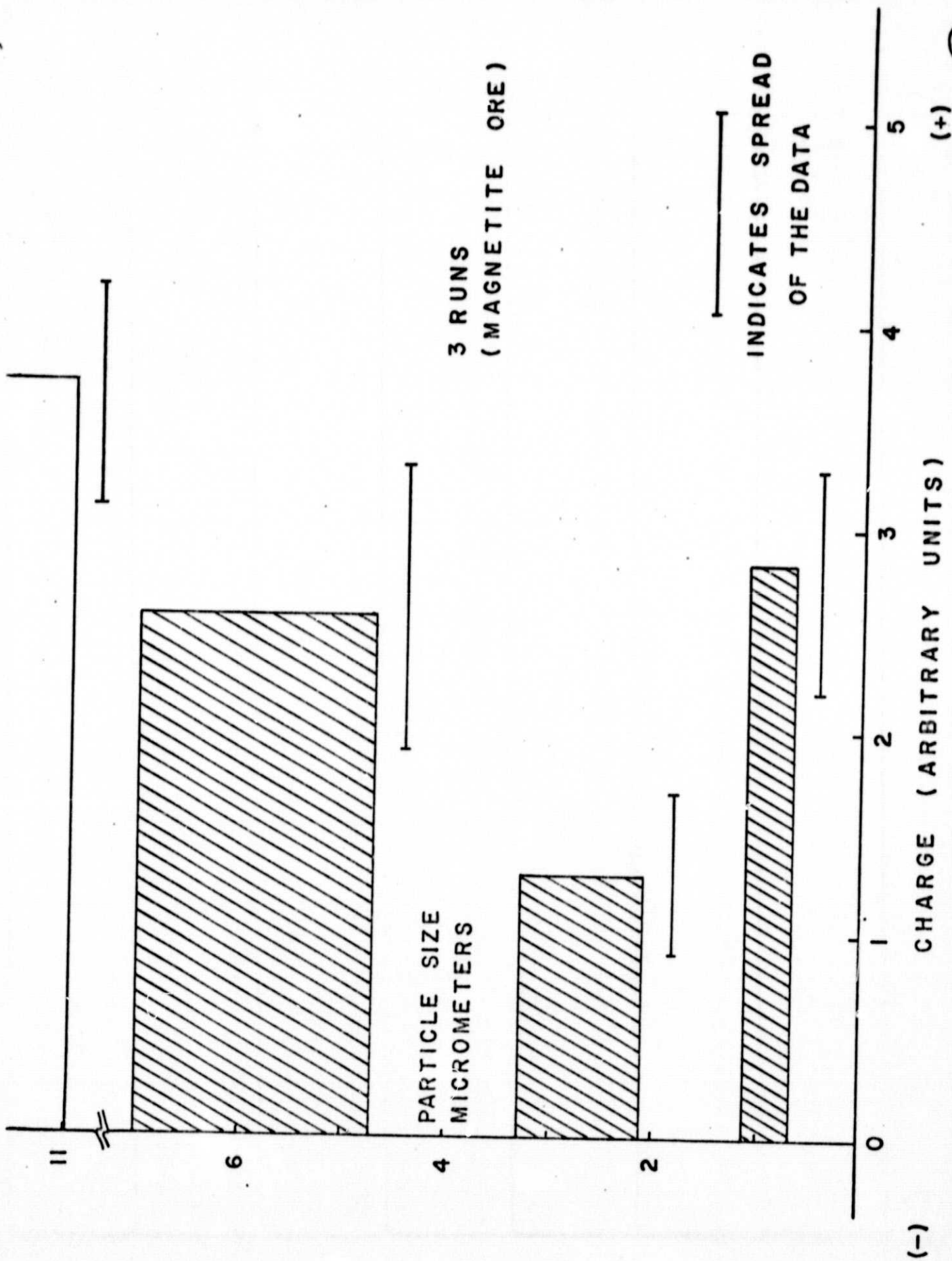


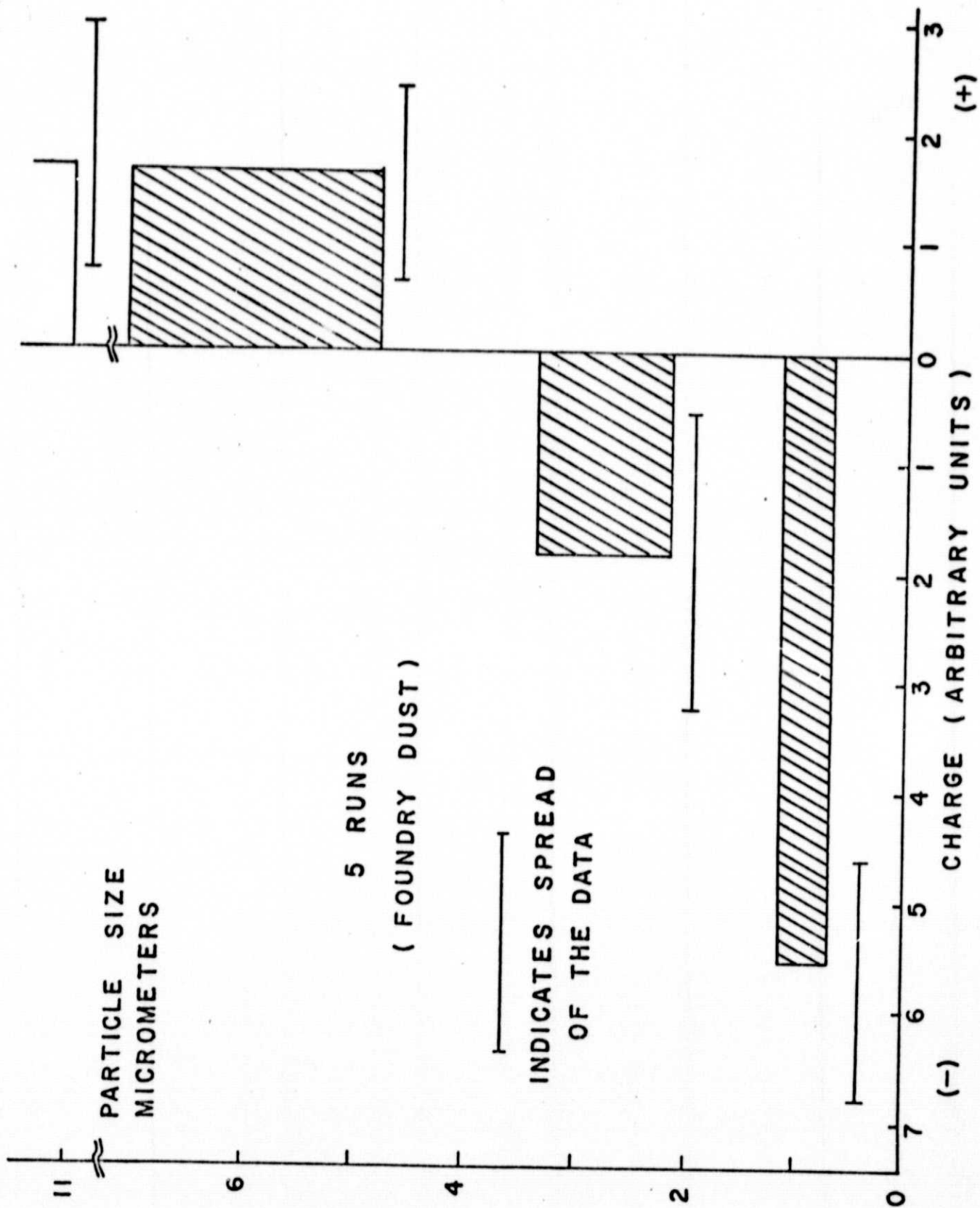


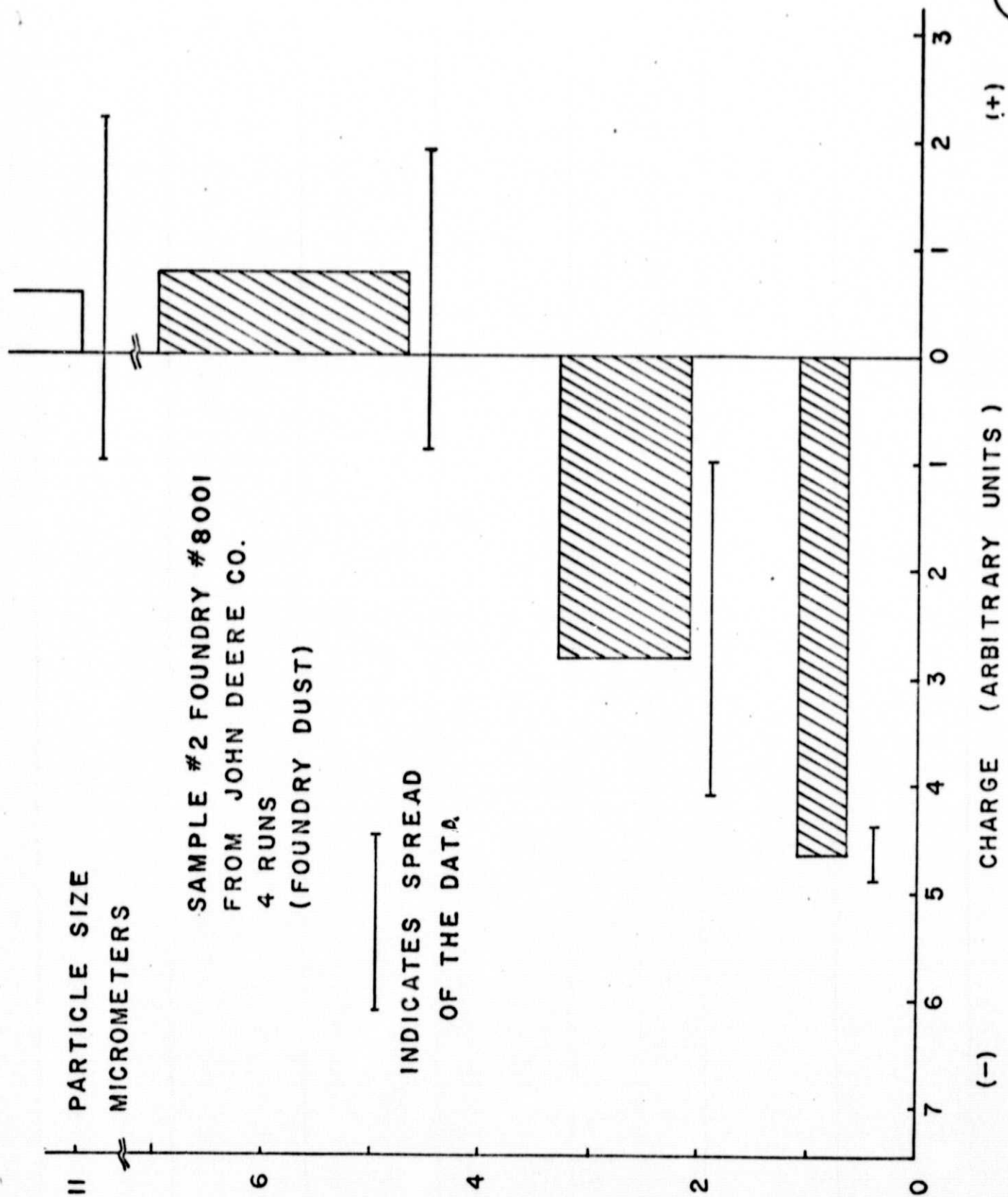


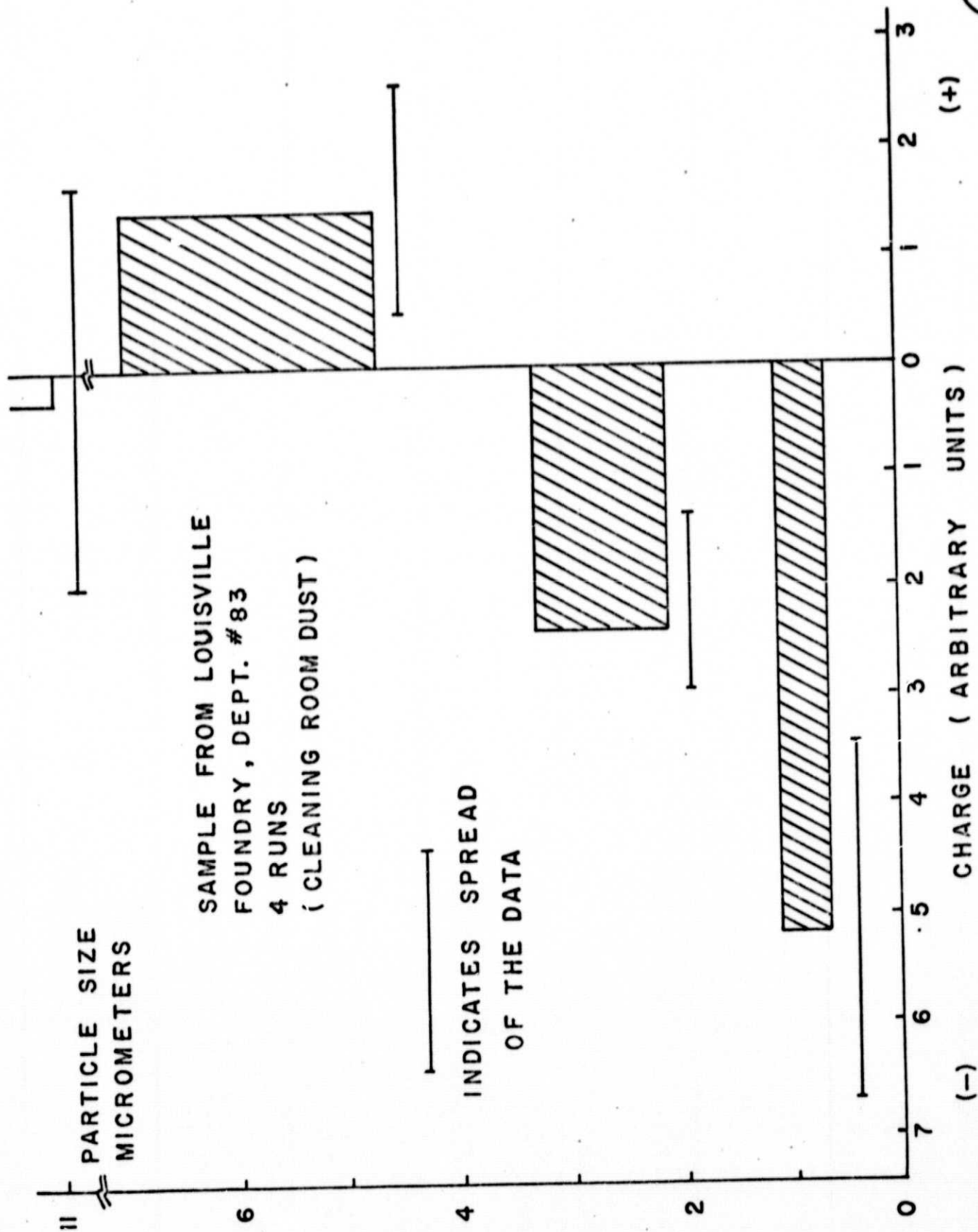


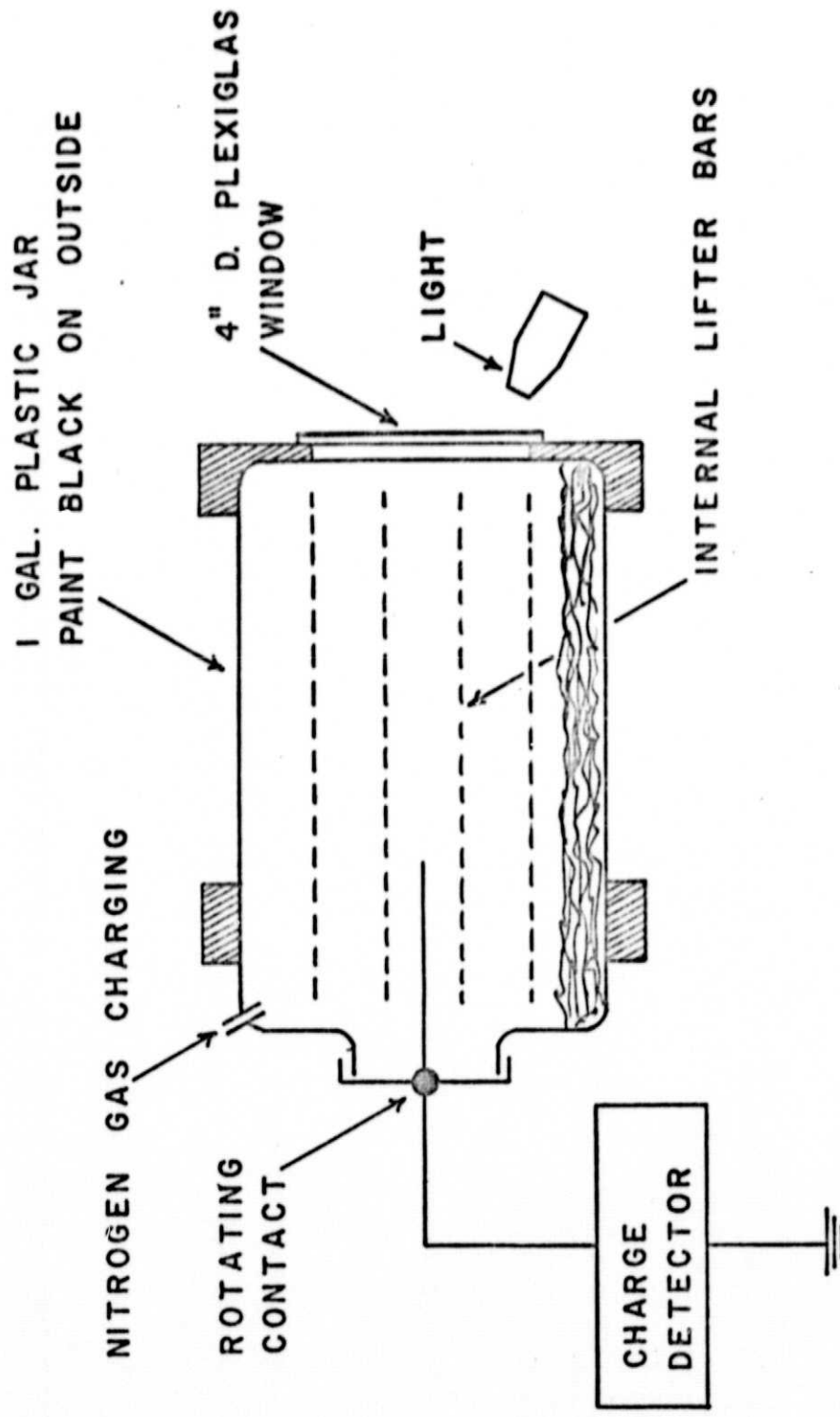




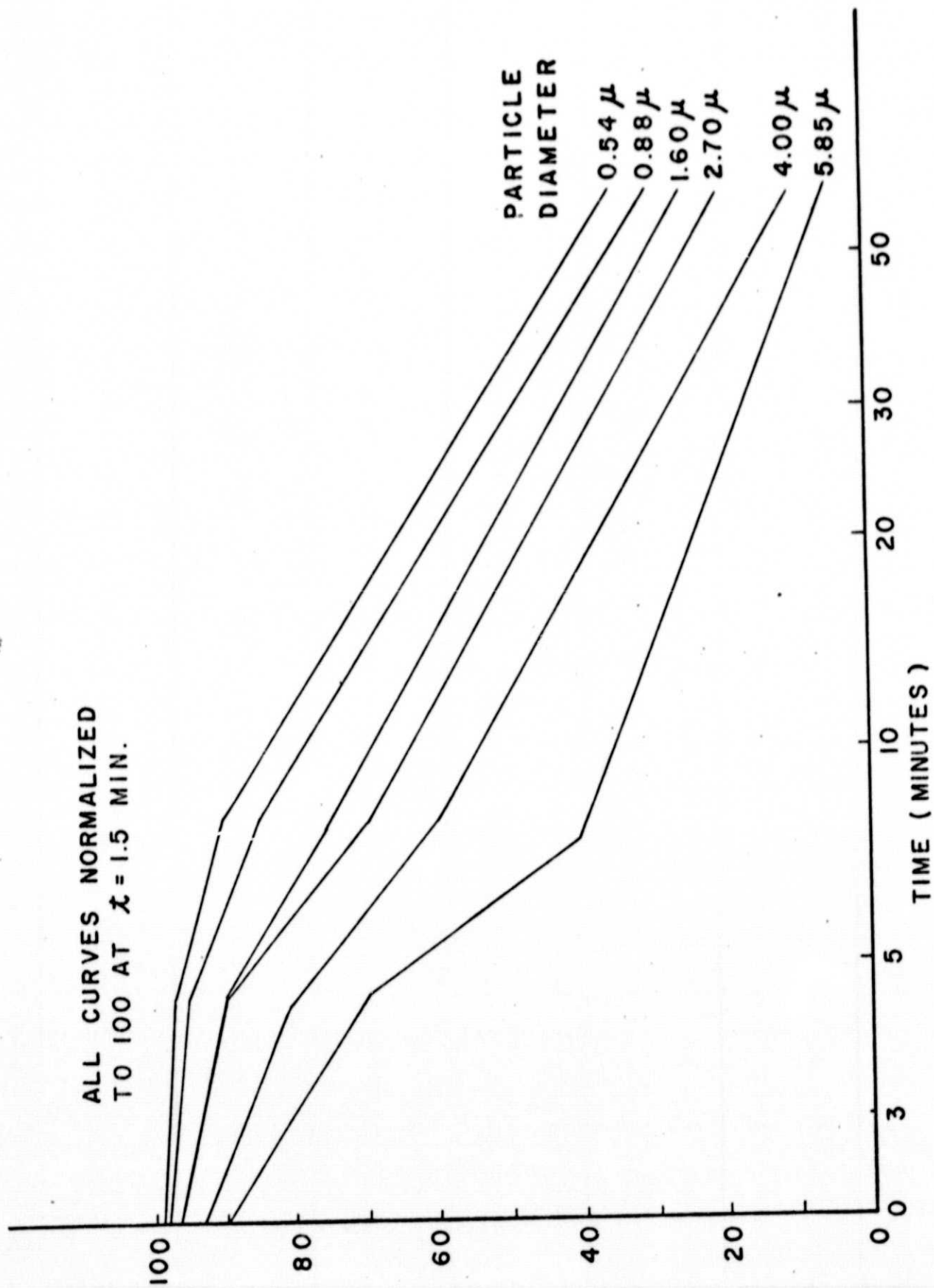




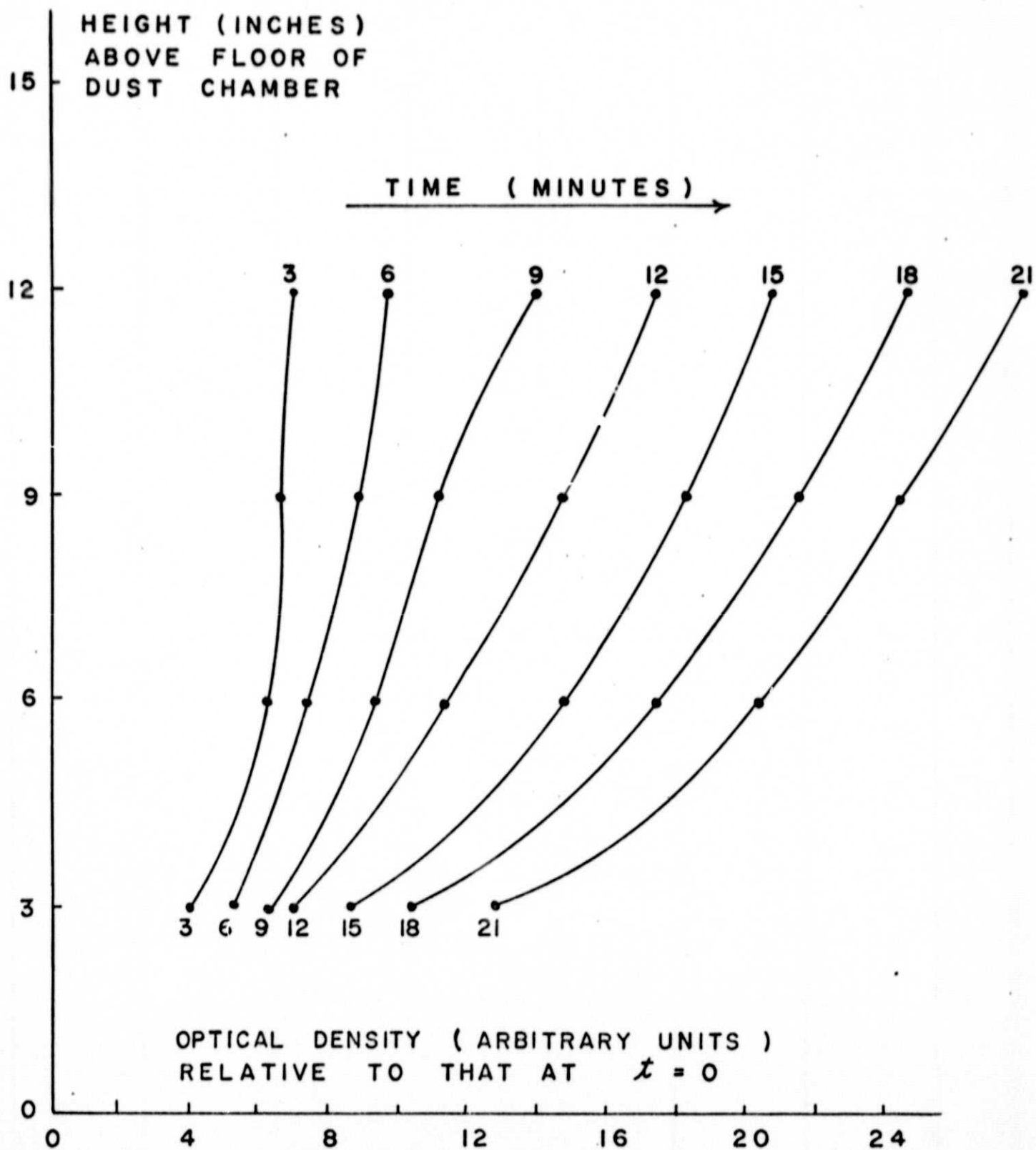




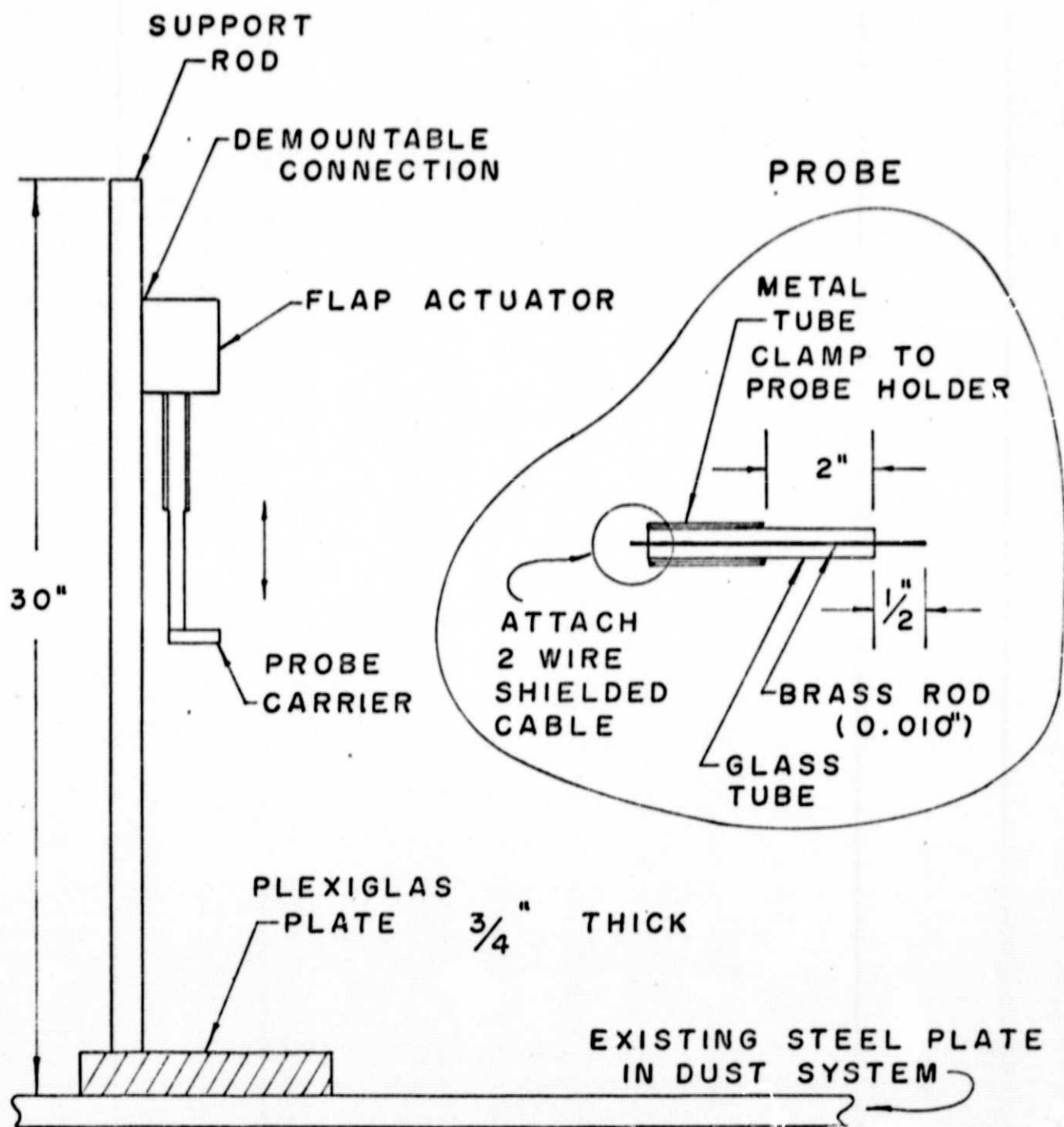
DUST CHARGING SYSTEM (SCALE NONE)



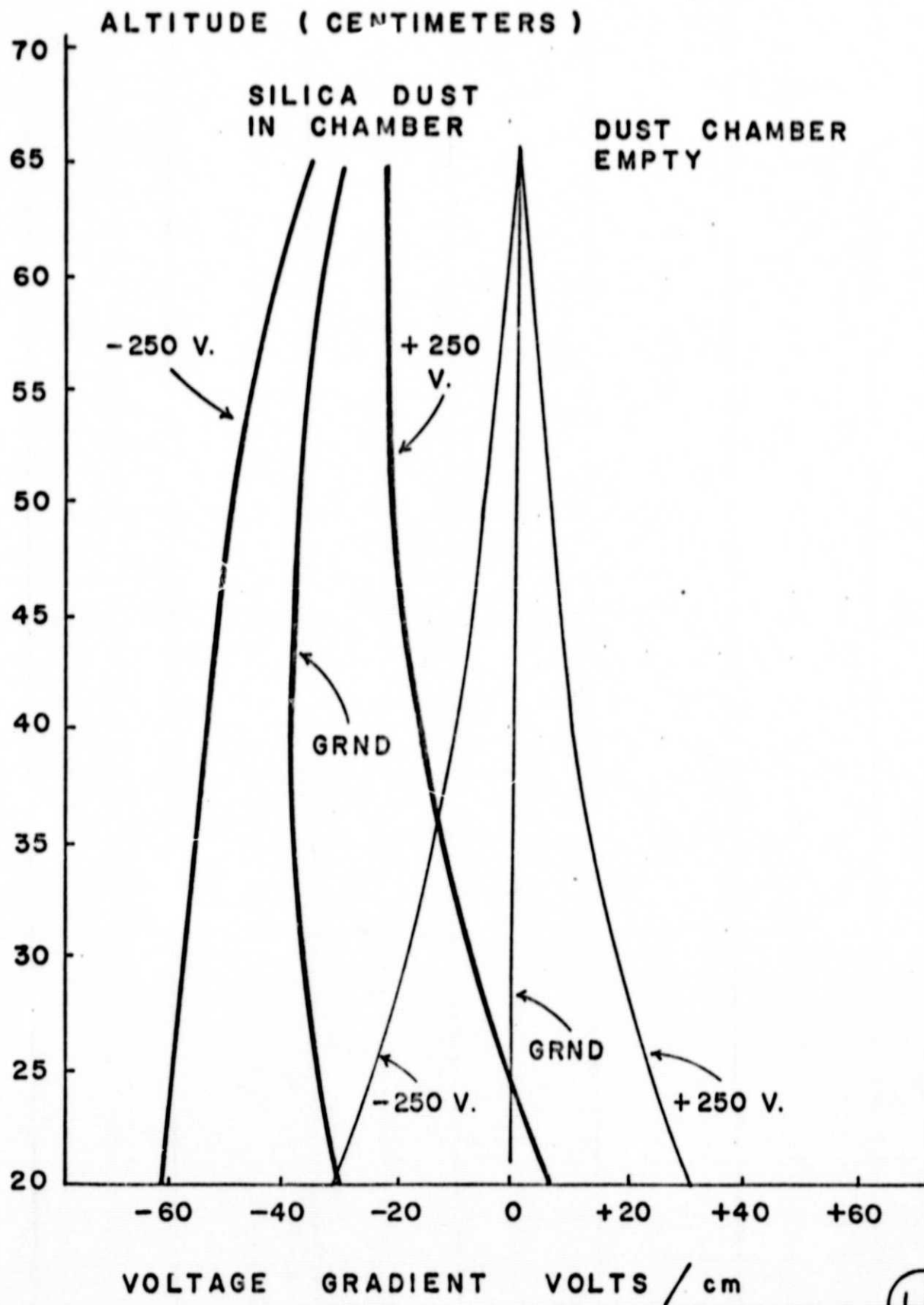
RELATIVE PARTICLE DENSITY VS SIZE AND TIME AFTER INJECTION
(SILICA SAND)

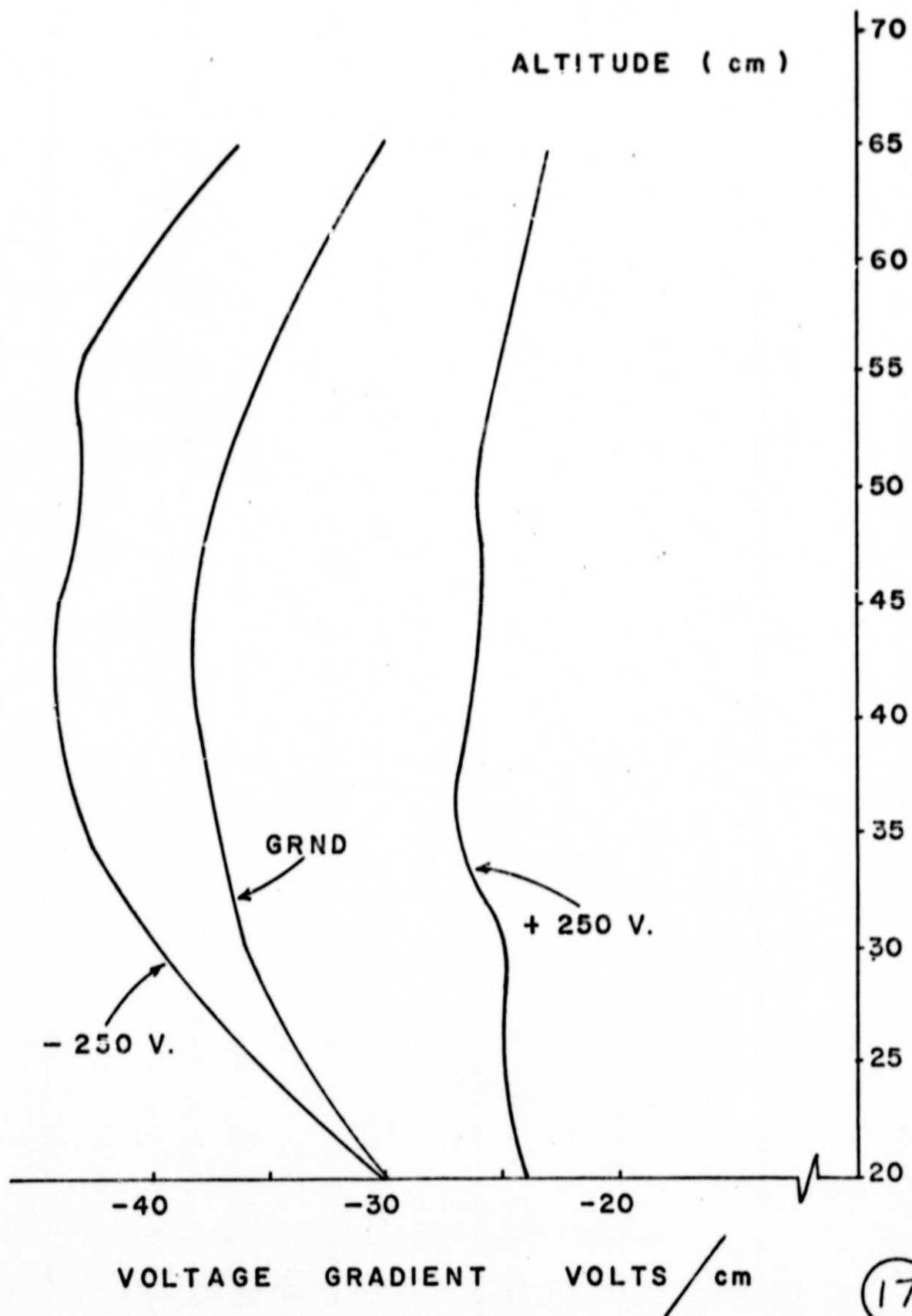


OPTICAL DUST DENSITY VS HEIGHT AND TIME AFTER
INJECTION (SILICA SAND)

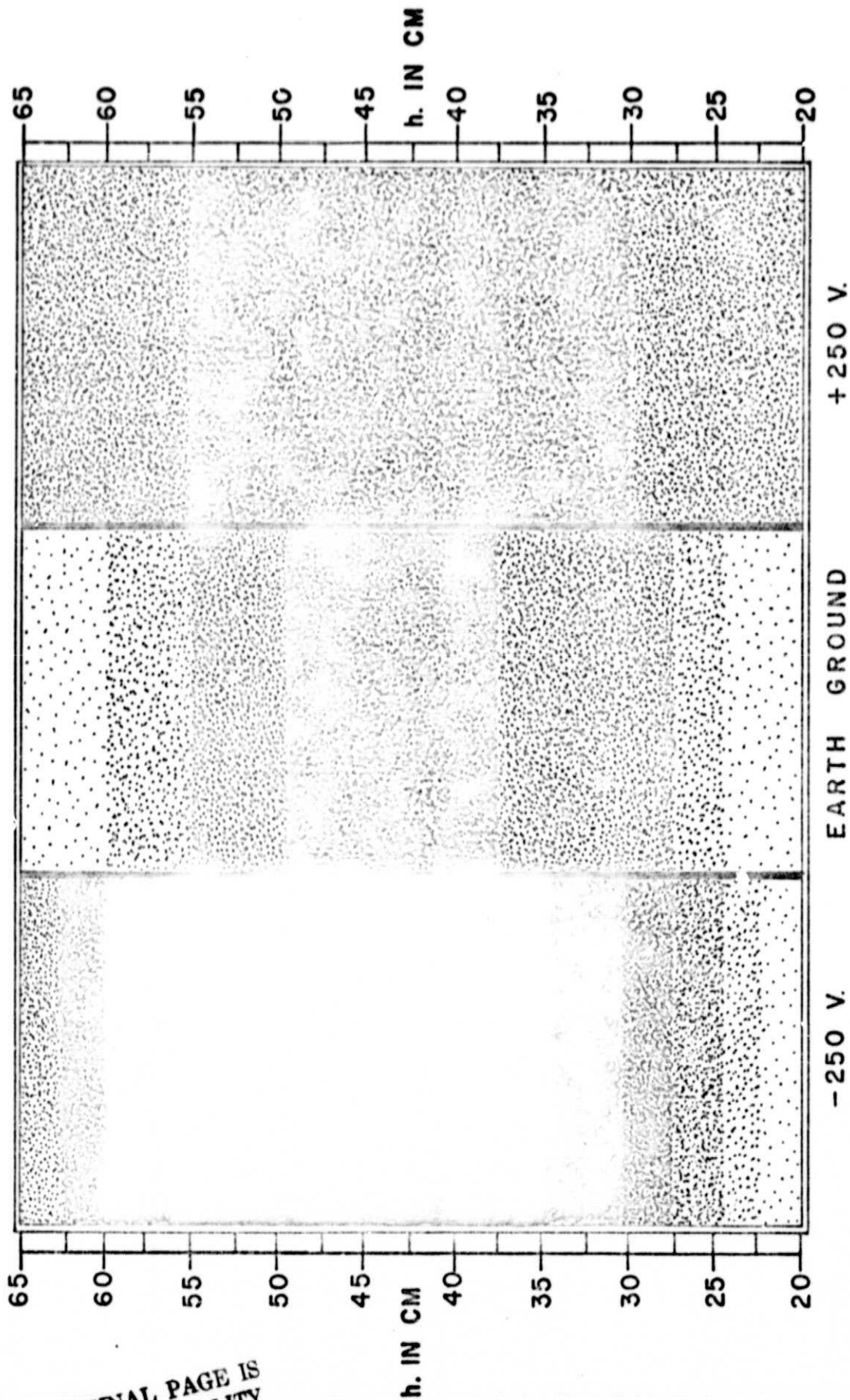


DUST CHARGE SCANNING SYSTEM

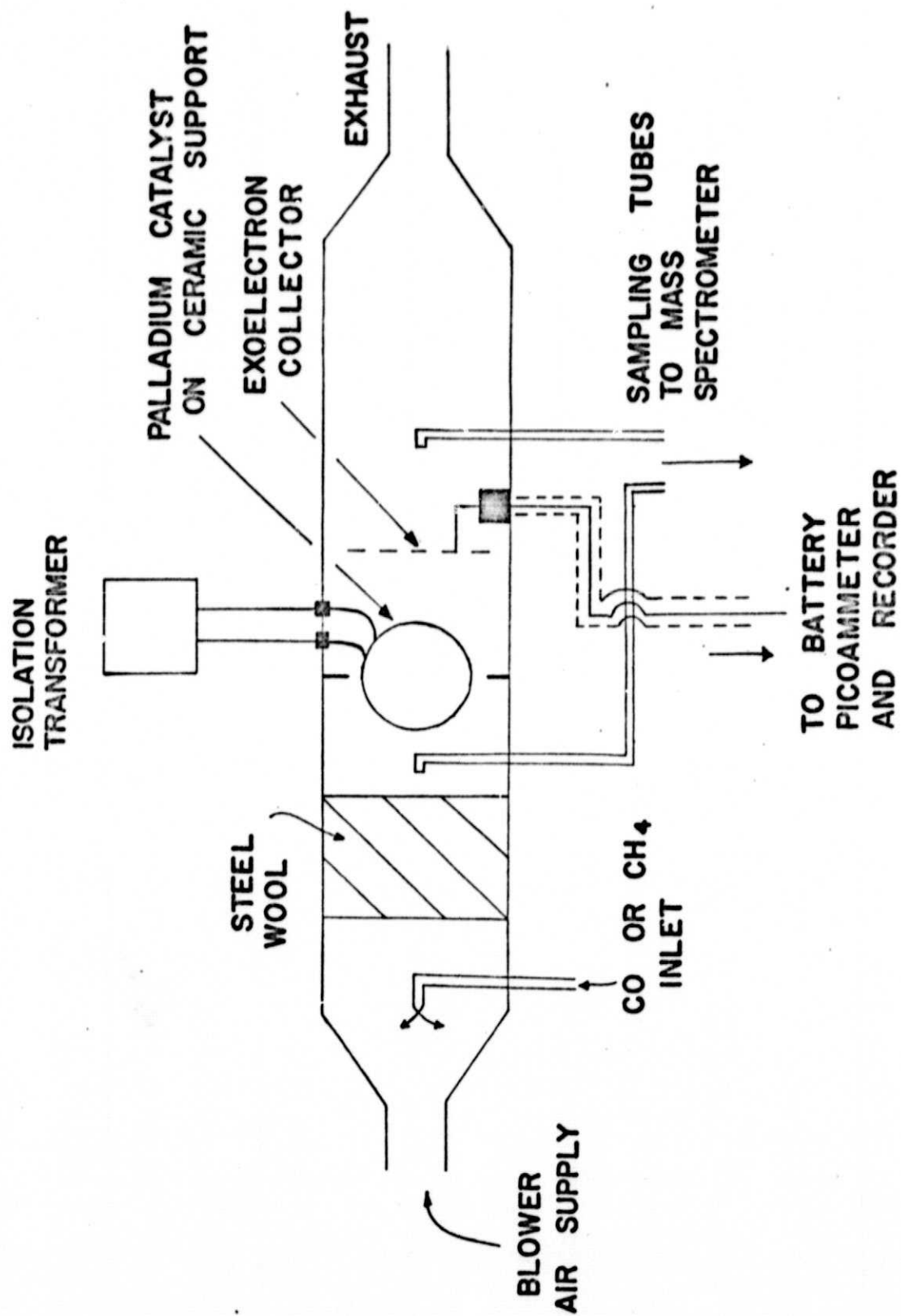


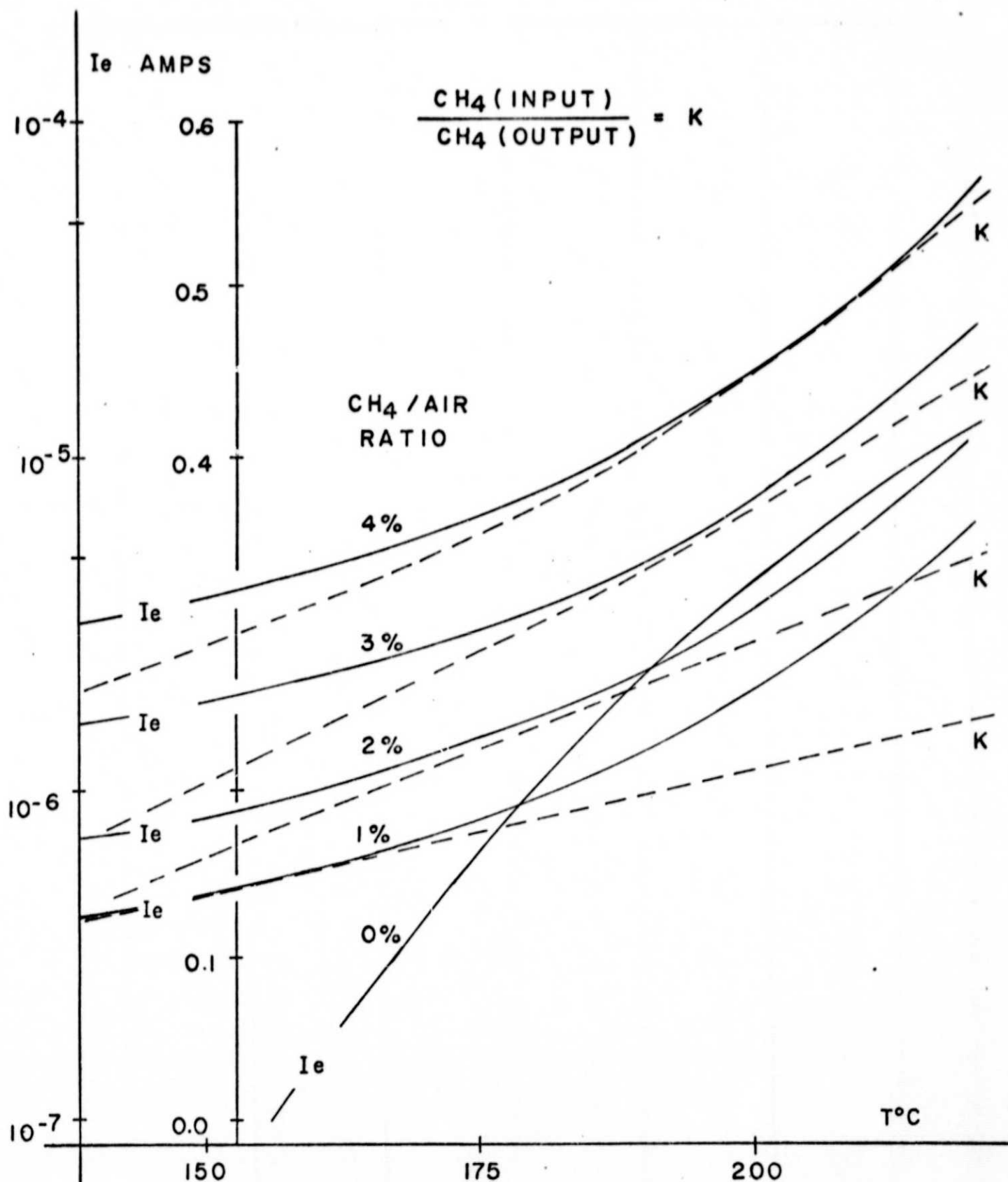


DUST DENSITY VS. HEIGHT : SILICA DUST CLOUD

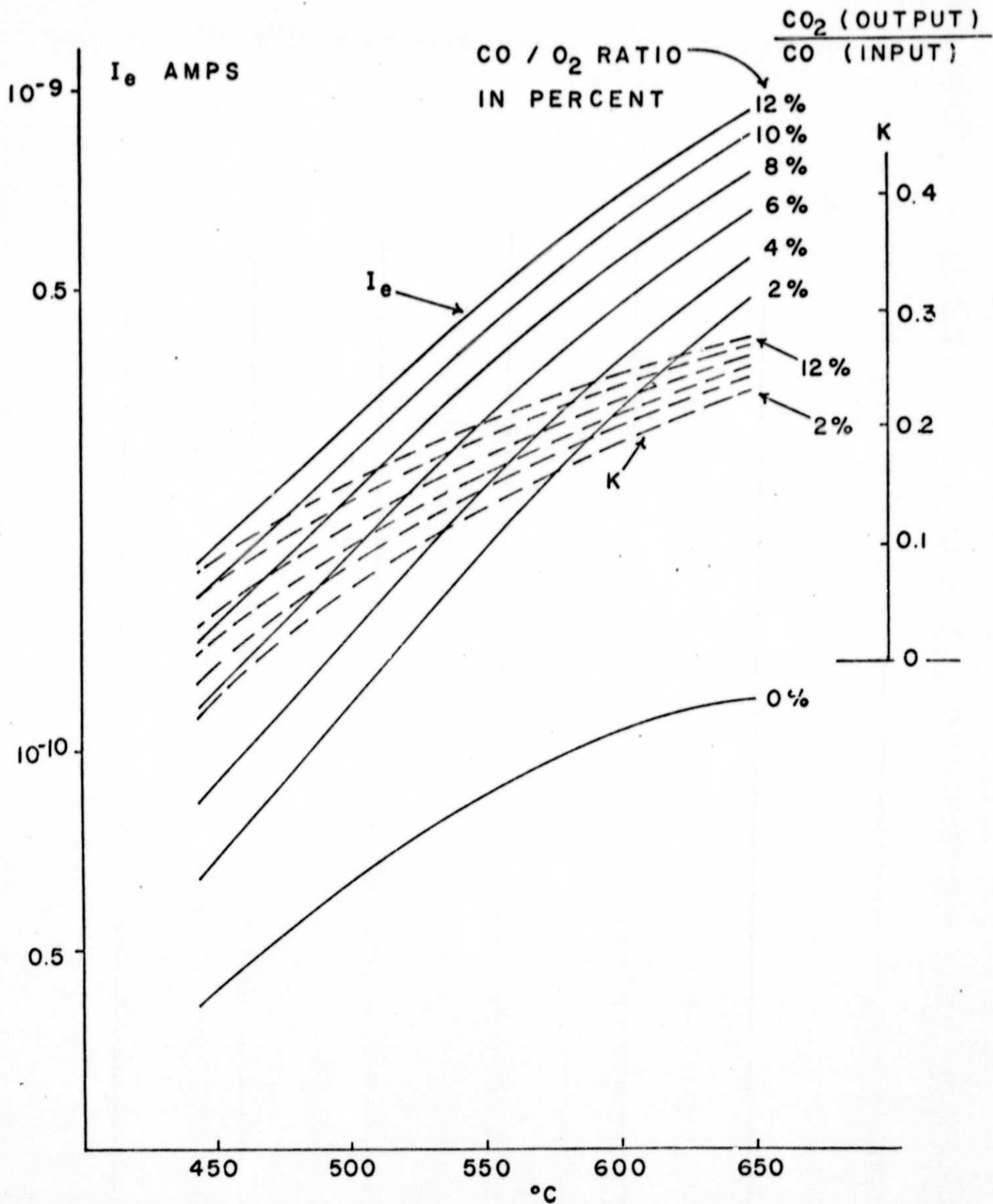


ORIGINAL PAGE IS
OF POOR QUALITY



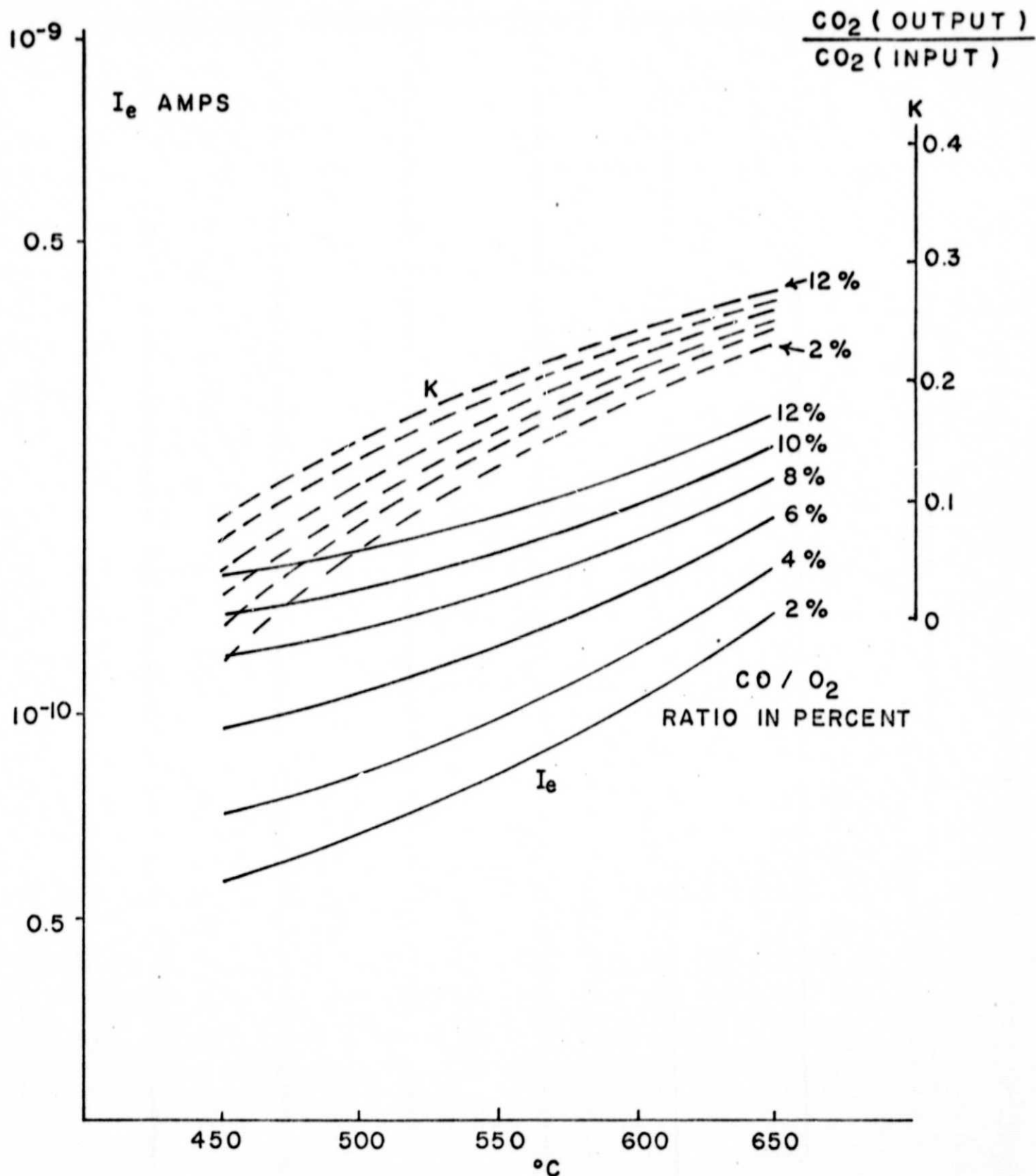


EXOELECTRON CURRENT AND REACTION COEFFICIENT VS TEMPERATURE AND PERCENT CH_4 IN AIR



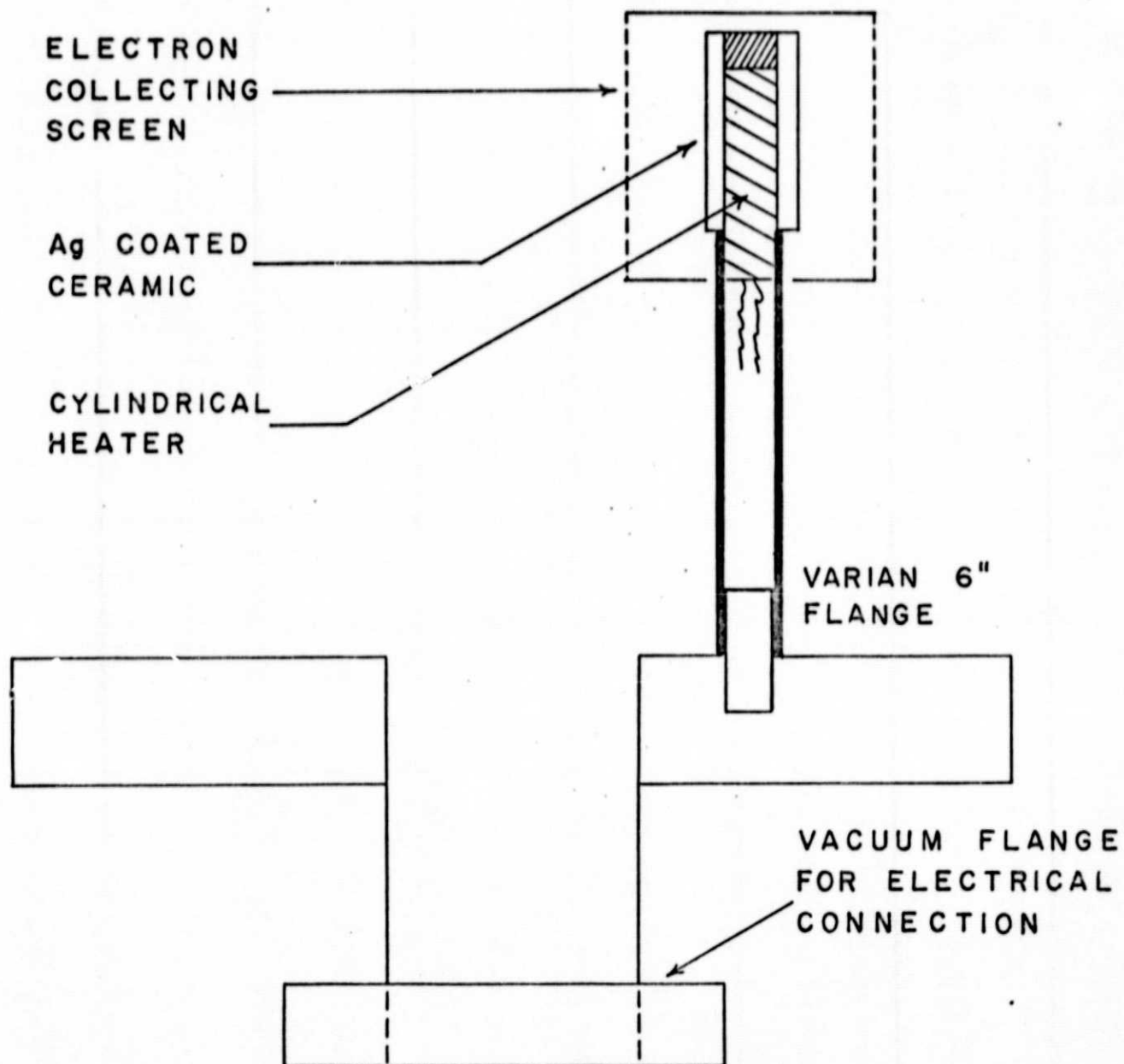
EXOELECTRON CURRENT (I_e) AND REACTION RATE (K) VS TEMPERATURE AND CO / O_2 RATIO

(RAW DATA)



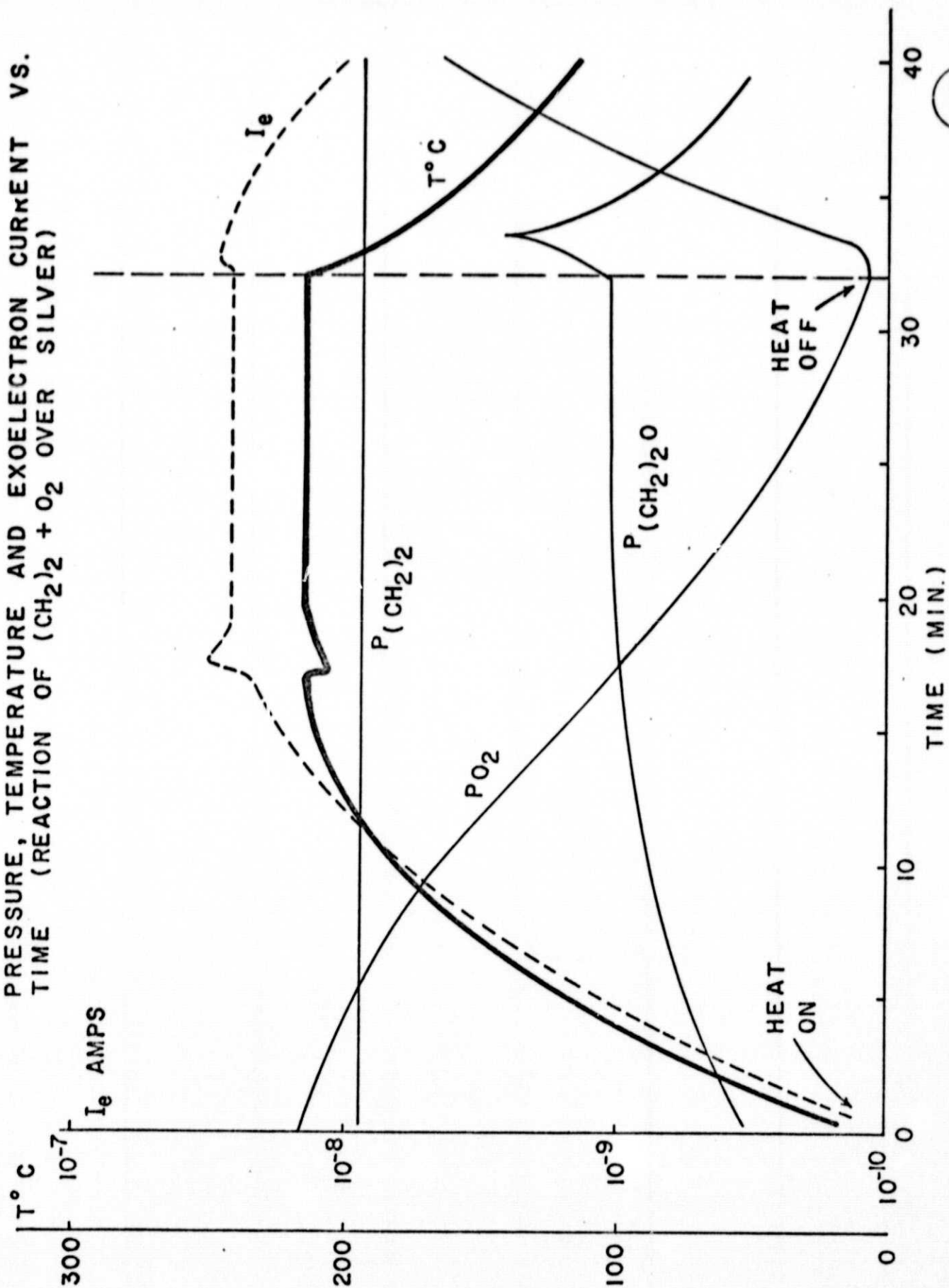
EXOELECTRON CURRENT (I_e) AND REACTION RATE (K) VS TEMPERATURE AND CO / O_2 RATIO

(REDUCED DATA)

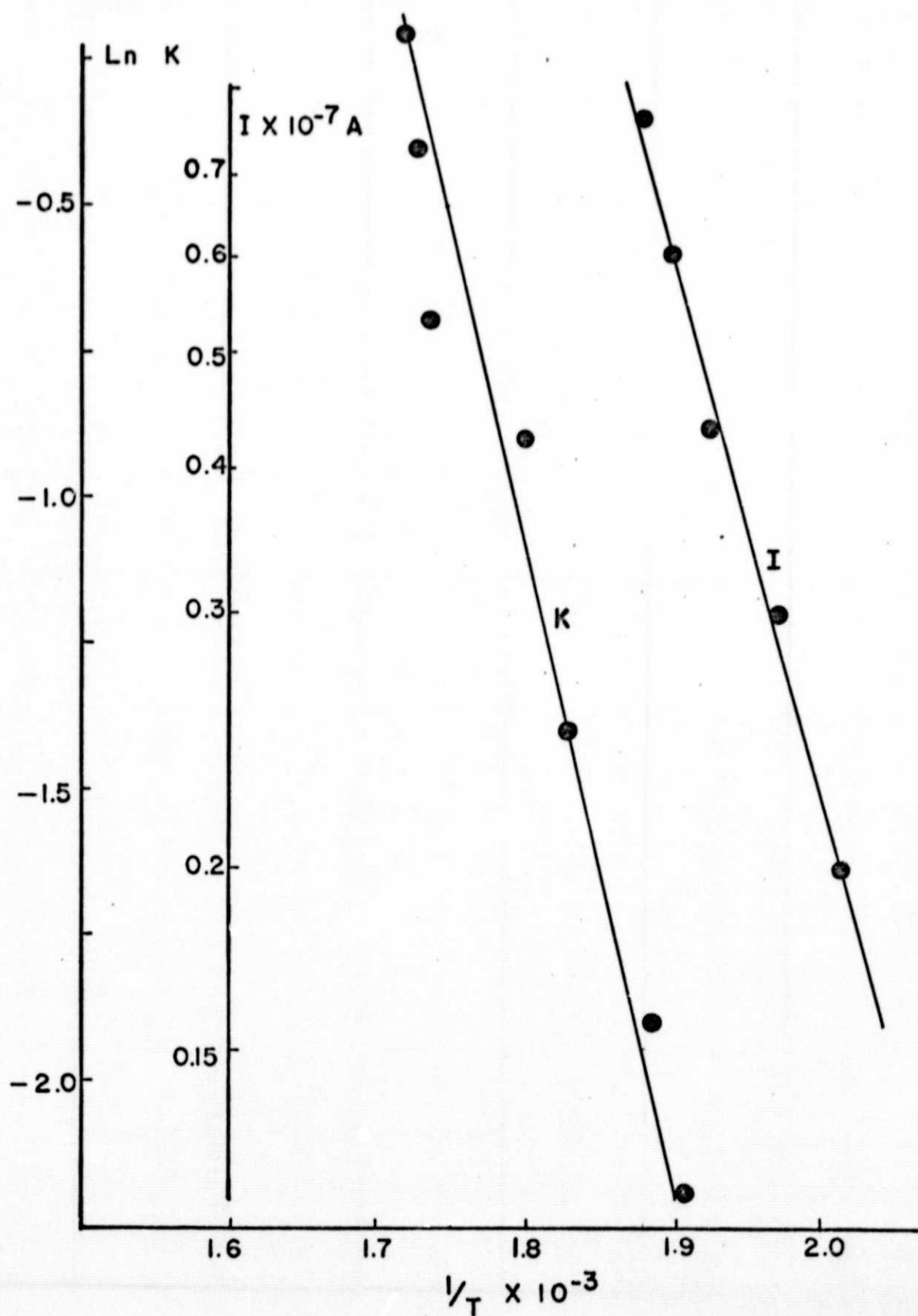


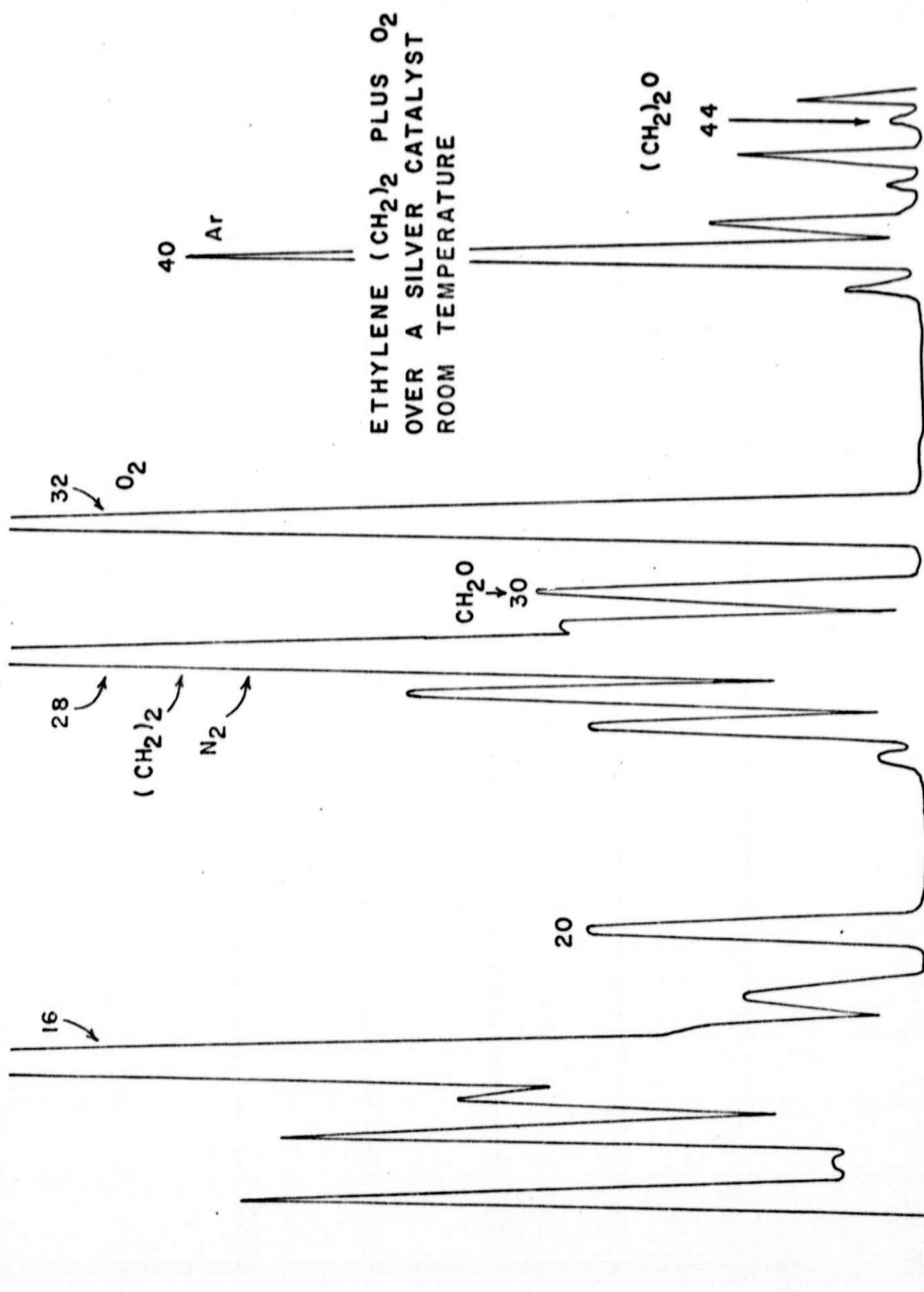
DISPERSED CATALYST EXPERIMENTAL SYSTEM

PRESSURE, TEMPERATURE AND EXOELECTRON CURRENT VS.
TIME (REACTION OF $(CH_2)_2 + O_2$ OVER SILVER)

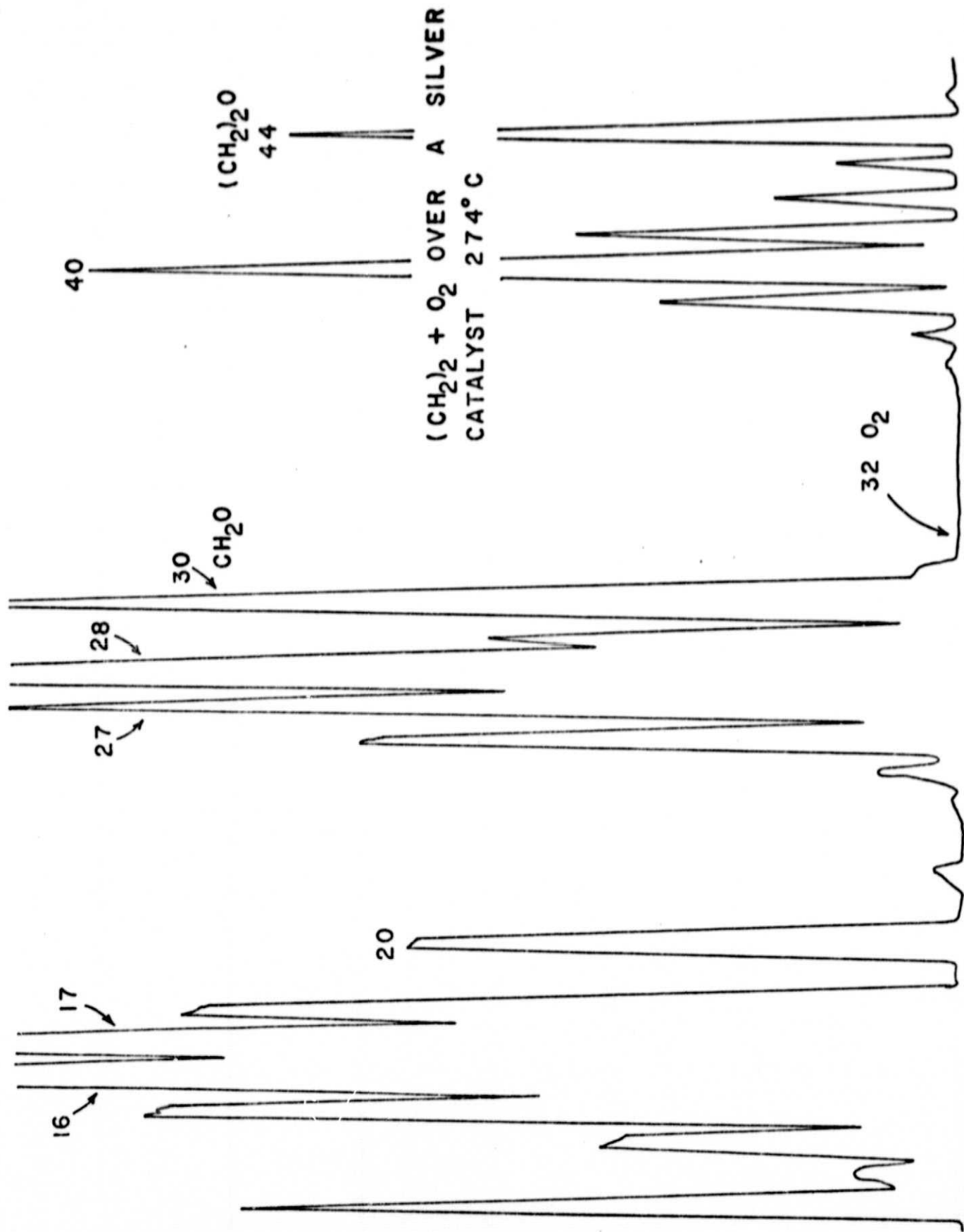


REACTION CONSTANT (K) AND EXOELECTRON
CURRENT (I) VS. TEMP. OXIDATION OF ETHYLENE
OVER A DISPERSED SILVER CATALYST





ETHYLENE $(\text{CH}_2)_2$ PLUS O_2
OVER A SILVER CATALYST
ROOM TEMPERATURE



m/e →